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Nest Placement of Nitrogen Fertilizers

by

© Carlos Maxwell Monreal Sepulveda

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF Master of Science

IN

Soil Fertility

Soil Science

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1981

THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled Nest Placement of Nitrogen Fertilizers submitted by Carlos Maxwell Monreal Sepulveda in partial fulfilment of the requirements for the degree of Master of Science in Soil Fertility.

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To My Parents
Hugo and Teresa

Ellos se declararon patriotas.
En los clubes se condecoraron
y fueron escribiendo la historia.
Los parlamentos se llenaron
de pompa, se repartieron
despues la tierra, la ley
las mejores calles, el aire,
la Universidad, los zapatos.

Pablo Neruda.
(Fragments of "Canto General")

To Marcia and Gilda

ABSTRACT

The present study was carried out to determine the effectiveness of N fertilizers placed in nests as a practical means to reduce N losses from fall applied N fertilizers. With the same objective, several N fertilizers were applied at different times during the fall. Laboratory incubations of soil samples were carried out to help confirm and explain the field results.

The results of field experiments at three locations showed that mineralization of soil organic matter occurred throughout the winter and, as a consequence, soils accumulated between 54 and 125 kg N/ha of mineral nitrogen before the spring thaw. An average of 41% of the mineralized soil N was lost during the spring thaw.

Forty-three percent of the urea-N applied in early fall and mixed into the soil was lost over the winter from the soil, but only about 13% was lost when the urea was placed in nests. The bulk of these losses occurred at the beginning of spring after thawing. Over-winter losses of urea-N were associated with lower yield responses to fertilizers added in the fall.

Thirty-eight percent of the urea-N applied in fall and mixed into the soil was nitrified by the first week of March, however, only 3% of the urea-N applied in fall and placed in nests, had been nitrified by the first week of March. Incubation studies of soil samples corroborated these results. When urea was placed in nests, its hydrolysis rate

was retarded and the growth of the nitrifying population, especially *Nitrobacter* sp., was inhibited.

It has been concluded that by slowing nitrification of nitrogen fertilizers applied in fall, the nest placement technique reduced overwinter N losses, resulting in higher yield and N uptake by barley.

Nest placement of N fertilizers appears to be a promising fertilization practice in western Canada and possibly in other places of the world. It may be an alternative to the use of chemical inhibitors to reduce N losses and to increase yield and quality of crops fertilized in fall.

The effect produced by different times of N fertilization during fall was of little importance relative to placing the N fertilizers in nests.

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1. INTRODUCTION

In the Prairie Provinces, fall application of N fertilizers has become an increasingly popular practice, and almost a quarter of the N fertilization is done by this time. Research conducted in Alberta, Saskatchewan and Manitoba in the last decade, has shown that fall applied N is often inferior (based on crop yield and N uptake) compared to spring applied N.

Nitrogen losses from the soil, occur mainly through leaching, runoff, denitrification and volatilization. Losses in Alberta appear to be mostly through denitrification.

Several approaches have been used to minimize these losses. Fertilization practices such as split applications, band placement and different times of fertilizer application have been tried. Also chemical inhibitors of nitrification and N sources of low solubility such as coated N fertilizers have been tested. However, the use of these compounds may be costly to the farmer.

Other practices, such as those used in paddy soils, include the application of concentrated N fertilizer formed into mud balls that are placed in the reduced layers of the soil. Fertilization practice with forests involve pellets of urea which are much larger than those found in conventional urea used for fertilizers. Apparently, in parts of Africa and India, for corn or for other hilled crops, each hill receives one "nest" of fertilizer. The nest is achieved by forming a neat vertical hole, and the fertilizer

(weighing several grams) is poured in the hole.

On the Canadian northern Prairie Provinces, losses with fall applied N are substantial, with fall application often reduced to two-thirds of the efficiency with the spring application, (efficiency meaning the amount of increase in crop yield or crop uptake of N). However, the different approaches to reduce losses of fall applied N have not been thoroughly studied in the Prairie Provinces.

The present investigation had the following objectives:

1. To test the hypothesis that nest placement of fall applied N will reduce losses of mineral N and consequently enhance the efficiency of fall applied N-fertilizers at three places of central Alberta.
2. To test the hypothesis that time of application and type of N fertilizer would influence the efficiency of fall applied N.

2. LITERATURE REVIEW

2.1 Nitrogen losses from soil.

Losses of soil N and fertilizer N have been detected in some areas of western Canada (Malhi, 1978). Net N losses have been shown to occur from the native organic pool after intensive cropping and poor soil management (Rennie et al., 1976). Also N fertilizers have been reported to be less efficient when applied in the fall than in spring (Malhi, 1978).

Newton et al. (1945), determined losses of carbon and nitrogen at eighty five locations across the prairies by comparing paired virgin and cultivated soils. They reported that after 22 years of cropping, the Black, Dark Brown and Brown soils had lost, on the average, 20% of the carbon and 18% of the nitrogen from the top 15 cm of soil; losses of C and N were about 30% from Gray soils. At some locations, they were as high as 50%, while at others there were apparent gains. Losses from the 15 - 30 cm segment were relatively small. From an agronomic point of view, it is important to analyze the extent to which different mechanisms affect losses of N from soils (especially those occurring in the Prairie Provinces), and also to suggest practical tools to overcome or minimize these losses.

Nitrogen is subject to continual non-harvest loss in soil, through processes such as leaching, erosion, fixation, immobilization, volatilization and denitrification, which

constitute a serious wastage of vital soil and fertilizer N (Hausenbuiller, 1978).

2.1.1 Erosion

Erosion is especially serious because it carries away organic matter that is a major source of soil N and other nutrients, causing a decline in both the quality and quantity of vegetation. Furthermore, runoff and erosion debris from grazing lands have increased the destructiveness of floods and added to silting problems of reservoirs and irrigation works. Also, this problem plagues those areas lacking a protective plant cover and where the precipitation is intense and winds are high (Stallings, 1957).

Wind erosion is probably the greatest problem in western Canada. Some soil removal, particularly on summerfallow, takes place throughout the year in much of the southern prairies (Johnson and Hennig, 1976). "Loss of top soil by wind and water erosion has been particularly serious in the medium and light textured soils and could account for a significant portion of the 40 million tons of N mineralized from the Chernozemic soils in western Canada during a 22 year period" (Rennie et al., 1976).

2.1.2 Leaching

Leaching losses of N involve nitrates for the most part and are common where excess water percolates through the soil (Allison, 1955). Nitrate distribution and leaching have

been mathematically interpreted, based on ion convection phenomena (Gardner, 1965).

Fall application of nitrogen for crops to be planted the next spring offers considerable potential for leaching loss, especially in humid areas. Percolation losses are generally greatest in the spring prior to rapid growth (Nelson and Uhlund, 1955). Land use practices in western Canada which involve substantial acreages of summerfallow have resulted in much deeper penetration of precipitation than was possible prior to cultivation (Rennie et al., 1976). Mychalyna (1959), in Manitoba, found up to 225 kg of nitrate-N/ha between 1.2 and 1.8 m depth in plots in a crop-fallow rotation. The amount of nitrate-N in the subsoil decreased as the frequency of fallow in the crop rotation decreased.

High concentrations of nitrate-N have been found below the rooting depth of crops on the University of Saskatchewan Goodale farm; the total nitrate-N to a depth of 4 m averaged approximately 500 kg N/ha. A two year rotation of fallow-wheat was followed on these loam soils for a period of about 40 years (Rennie et al., 1976). It is unknown how much nitrogen resides presently below the 3 to 4 m depth in Saskatchewan, however, Meneley (1976), working in the Moose Jaw area, suggests that it is probably safe to assume that substantial amounts of nitrate-N will be found at greater depths. He suggested that crop removal and leaching losses together may account for approximately 50% of the N released

from the soil organic matter in Saskatchewan. However, Field-Ridley (1975), applying 550 kg N/ha as ammonium sulfate and urea to a loam and a clay soil, found that movement of nitrate-N below the zone was negligible over a two year period.

Malhi (1978), showed that leaching losses of N in north-central Alberta were of little significance during and after early spring thaw, when large losses of mineral N occur.

Since cultivation, Canadian prairie soils have mineralized from the organic pool approximately 85 million tonnes of N (Rennie et al., 1976). Approximately 30% of this nitrogen was removed by the grain of the various crops grown, and perhaps 20% has been leached below the rooting depth of annual crops. Leaching losses have probably been greater in Saskatchewan than in either Alberta or Manitoba, a direct reflection of the high frequency of summerfallow that has been prevalent in the former province for several decades (Rennie et al., 1976).

Ridley and Hedlin (1968), found that frequent summerfallowing resulted in the greatest decline in organic matter and total N. In my opinion, soils provided with optimum N fertilizer practices can be expected to remain with their N content relatively constant. However, if present land use practices continue (summerfallow), the nitrogen content of soils will continue to decline (personal communication).

2.1.3 Ammonium and ammonia fixation

Both the inorganic and organic soil fractions have the ability to fix ammonia and ammonium in forms relatively unavailable to higher plants or even microorganisms (Brady, 1974; Nyborg, 1969). The mechanism of ammonium fixation by soil colloids is similar to that of potassium fixation. Ammonium ions replace interlayer cations in the expanded lattices of clays minerals such as Vermiculite, Illite and Montmorillonite (Walsh and Murdock, 1960).

Jahn (1971) reported that a wide range of cultivated soils in the Dark Brown, Black and Gray Wooded soil zones in central and northern Alberta, had very low capacities to fix added ammonium (less than 7% on the average), and only rarely did this capacity exceed 100 ppm of NH_4 (about 32% on the average). Sowden et al. (1978), studying the ammonium fixation capacity of eastern Canada soils, found in general that the amount of fixed ammonium was related to the content and type of clay, and this capacity increased down the profile. The amounts fixed ranged from 12 to 450 μg of fixed native $\text{NH}_4\text{-N/g}$ soil. The capacity to fix added ammonium was usually low in the sandy soils. Cultivated soils of New Brunswick had low ammonium fixing capacities.

Kowalenko and Cameron (1978), using N^{15} in a clay loam soil near Ottawa, determined that the soil clays fixed 34 to 60% of the 150 kg NH_4 /ha fertilizer immediately upon application. However, 71 to 96 % of the fixed ammonium became available to barley during the growing season.

The fixation of ammonia is linearly correlated with the percentage of carbon in the organic matter and the mechanism is not completely understood, although it is suggested that hydroxyl groups of the organic matter may be the sites of the reaction with the added ammonia (Burge and Broadbent, 1961). Soil humus and forest litter fixed 2 to 7% N by weight from aqueous ammonia (Mattson and Koutler-Anderson, 1943) and organic soils fixed an average of 160 meq gaseous ammonia per 100 g of C content (Burge and Broadbent, 1961).

Nyborg (1969), reported that organic soils of Quebec fixed from 39 to 190 meq ammonia per 100 g, while mineral soils of Alberta and Saskatchewan fixed 2.5 and 8.5 meq, respectively. The organic matter in air dried soils did not fix gaseous NH_3 from light applications that gave little increase in soil pH.

2.1.4. Internal N cycling

From an agronomic point of view, the balance between mineralization and immobilization of N in soils controls the supply of available N and other nutrients to crops. Nitrogen is the most important element in soil organic matter, when considered from the economic standpoint (Allison, 1973).

Mineralization and immobilization (turnover of N), proceed simultaneously, and in opposition in soils (Campbell, 1978). Because microbiological immobilization is determined by the utilization of nutrient elements for cell synthesis, the magnitude of immobilization is proportional

to the net quantity of microbial tissue formed and is related to carbon assimilation by a factor governed by the C/N, C/P, C/K or C/S ratio of the newly generated protoplasm (Alexander, 1977). The above ratios vary with growth rate, substrate supply and environmental conditions (McGill et al., 1981). Iritani and Arnold (1960) found that N mineralization equals N immobilization during decomposition of residues having a C/N ratio of about 22 and about 2% N; larger or smaller ratios are associated with net immobilization and net mineralization, respectively. These values are obviously not constant and depend on several factors, including temperature and time allowed for turnover, the supply and kind of mineral N in the soil, the amount and composition of the organic substrates (Campbell, 1978); aeration, moisture content and pH (Harmsen and Van Schreven 1955; Harmsen and Kolenbrander, 1965).

Mineralization is very slow near the freezing point because of restricted microbial activity. Ammonification continues over a considerable range of temperatures above 35 C, but nitrification ceases at 45 C (Harmsen and Kolenbrander, 1965). Below the optimum temperature, which varies between 20 and 45 C depending upon climate (Malhi and McGill, 1981), nitrification decreases gradually following an asymptotic curve and practically ceases near the freezing point (Sabey et al., 1956). However, comparatively vigorous nitrification at temperatures near the freezing point was reported by Tyler et al. (1959). Ammonification continues

below 0 C (Tret'yakova, 1977). Malhi and McGill (1981), reported nitrification of ammonium sulfate, ($0.02 \text{ ug N g}^{-1} \text{ d}^{-1}$), in three soils of Alberta that were incubated at -4 C. Malhi (1978) and Malhi and Nyborg (1979b), detected a net mineralization of the native soil organic matter and nitrate accumulation from fall applied urea during winter in frozen soils of Alberta.

A combination of soil moisture, 50 > 70%, and a temperature of about 2 C, was most favorable for the development of the principal groups of aerobic microorganisms and accumulation of enzymes and certain vitamins in podzolized chernozem of the Cis-Urals Region (Khaziev, 1977).

In an experiment with N^{15} , about one fifth of the N was immobilized during winter from fall applied KNO_3 , urea and $(\text{NH}_4)_2\text{SO}_4$. The rate of mineralization was approximately equal to the rate of immobilization (Malhi, 1978).

Immobilization of fall applied fertilizer N, and its subsequent remineralization, may provide little N to the first crop. However, fertilizer N immobilized and its rate of re-mineralization over the years is important in determining long term effects on soil receiving repeated fall applications of N (Nyborg and Leitch, 1979).

2.1.5 Gaseous N losses

2.1.5.1 Volatilization of N as ammonia

Ammonia volatilization losses can occur from soil surfaces when ammonia is applied as fertilizer or is formed near the surface, and when the adsorption capacity of the soil is not sufficiently large to hold the ammonia (Harmsen and Kolenbrander, 1965). Free ammonia escapes when ammonium salts react in alkaline aqueous media (Tisdale and Nelson, 1975). If fertilizer salts containing ammonium-N are placed on the surface of alkaline soils, free ammonia is lost (Carter and Allison, 1961; McGill, 1971). These losses are aggravated by high soil temperatures and rapid evaporation of water. They can be prevented by placing the N materials several centimeters under the soil surface (Rennie et al., 1976; Tisdale and Nelson, 1975).

A Losses of ammonia from urea applied to soil surfaces, take place regardless of soil pH. Similar losses can be obtained from applications of ammoniacal compounds that are sources of fertilizer N. For example, anhydrous ammonia may be lost to the atmosphere during and after application. Factors associated with this loss are the physical conditions of soil during application, soil texture, soil moisture, depth and spacing of placement (McDowell and Smith, 1958). These gaseous ammonia losses are of universal occurrence (Aggarwal and Kaul, 1978; Connell et al., 1979; Heber et al., 1979).

2.1.5.2 Denitrification losses

The reduction of oxidized forms of N with the production of N gas (N_2) or some of the volatile oxides of nitrogen, may be a mechanism of considerable importance to deplete part of the soil N and fertilizer N reserve. The sequence of steps involved in the reduction of NO_3 to nitrogen gases is known as denitrification (Campbell and Lees, 1967). Only a small number of facultative anaerobic bacteria can bring about denitrification. The active species are largely limited to the genera *Pseudomonas*, *Achromobacter*, *Bacillus* and *Micrococcuss*, although *Thiobacillus denitrificans* and an occasional *Chromobacterium*, *Mycoplana*, *Serratia* or *Vibrio* species will catalyze the reaction (Alexander, 1977).

Denitrification rates have been thought to be independent of NO_3 concentration (zero order kinetics) over a fairly wide range from 40 to 500 ppm NO_3 -N (Broadbent, 1951; Cooper and Smith, 1963). However, Bowman and Focht (1974), found denitrification rates to be substrate-dependent at lower concentrations approximating a first order reaction, and gradually diminishing at higher concentration (1000 ug NO_3 -N/ml) to become a zero order reaction.

Under low oxygen tension, nitrate is used as an alternate electron acceptor in place of oxygen (Campbell and Lees, 1967). Factors such as temperature, supply of available carbon and pH are all important to the rate of denitrification (Smid and Beauchamp, 1976; Burford and

Bremner, 1975; Nommik, 1956). In the denitrification process, nitrate is reduced first to nitrite, which is transformed to some unknown nitrogenous intermediate. The latter is probably converted to N_2 with N_2O as intermediate, but N_2 alternatively may be formed by a pathway not involving N_2O . Nitric oxide may be implicated as well (Alexander, 1977; Campbell and Lees, 1967). Some of the actual enzymatic mechanisms involved in this process are now reasonably well understood (Fewson and Nicholas, 1961).

Abundant references exist in the literature describing denitrification losses in studies conducted with field experiments. Doughty et al. (1954), in a study carried out from 1939 to 1950 to determine the loss of organic matter and nitrogen resulting from the breaking of native sod, reported losses of as much as 30% of the initial N over a period of eleven years. They emphasized that plant uptake could not account for all the N lost. They concluded that some of the N had been nitrified and the nitrates leached beyond the root zone. However, they assumed that most of the N which had not been accounted for had been lost through denitrification.

Campbell et al. (1975), concluded that more than 70% of the total N which was apparently mineralized in 35 years, could not be accounted for as grain and only 5% of the mineralized N was still present in the profile as NO_3^- -N. Doughty et al. (1954), set up controlled studies in the greenhouse where soils were watered periodically to bring

the soil to field capacity. With no possibility of leaching or plant uptake, any losses were assumed to be due to denitrification. After five years, soils were air dried and analyzed for total C and total N. It was found that soils lost about 18 to 24% of the C, with the virgin soils losing more than the corresponding cultivated soils. The losses of nitrogen under greenhouse conditions were much lower than found under field conditions for equivalent periods (5 to 9% over five years). Leaching and subsequent denitrification of nitrate-N has been shown to occur in a sandy lacustrine soil on which cattle had been confined (Partridge and Ridley, 1974). Field-Ridley (1975), found large losses of nitrogen when 550 kg N/ha were applied to field plots on a Red River clay soil. No leaching of nitrates was detected and losses were attributed to both immobilization and denitrification.

In Alberta, losses from soil N and fertilizer N have been reported to occur at the beginning of spring when the soil is completely saturated (Nyborg and Leitch, 1979; Malhi, 1978). The latter, using fertilizer N^{15} , found that N losses in early spring are almost exclusively through denitrification, and that nitrate-based fertilizers applied in fall were less efficient than ammonium-based fertilizers applied in fall. In his study, 39.3% of the $Ca(NO_3)_2$ applied in the fall was lost through denitrification as compared to 29.1% loss of N from urea and 16.1% loss of N from $(NH_4)_2SO_4$.

Nitrogen fertilizers applied in the fall in Manitoba and in northern and central Alberta have been consistently inferior to spring applied N fertilizers (Ridley, 1975; Nyborg and Leitch, 1979).

Although this short review shows that N losses in western Canada occur through most of the previously described mechanisms, denitrification would seem to be the main process causing loss of soil and fertilizer N from soils of Alberta. It is possible to establish proper soil and fertilization practices to control and maintain the level of soil N in the long run.

2.2 Controlling denitrification losses from soil

Since almost 25% of the N fertilization in Alberta is made during fall and 30% or more of the fertilizer N mixed into the soil is lost (Nyborg et al., 1977), it is important to enhance the efficiency of fall applied N fertilizers by developing and adapting new techniques to overcome or minimize denitrification losses produced from saturated soils in early spring. The subsequent review deals with the actual techniques being used today in agriculture to make the use of fertilizer N more efficient.

2.2.1 Use of chemical inhibitors

There have been several intensive surveys designed to find non-phytotoxic chemicals which would, by selectively

inhibiting the nitrifying bacteria, diminish nitrogen losses following fertilization; i.e., chemicals which would keep the element in a reduced form for longer periods than could be expected under usual field conditions (Alexander, 1977). A similar approach to this problem was advocated by Goring (1962). He believed that it was desirable to inhibit or eliminate the phenomenon of nitrification altogether.

The use of inhibitors with NH_4 -based fertilizers may reduce the loss of fertilizer N by leaching (Wagner and Smith, 1958) and by denitrification (Parker, 1972; Reddy and Prasad, 1975). Slowing nitrification of NH_4 -based fertilizers applied in fall may also be beneficial by eliminating NO_3 accumulation during winter (Nyborg and Leitch, 1979). Inhibitors also may reduce plant diseases (Huber and Watson, 1972).

Among the inhibitory compounds patented for use in connection with fertilizers containing ammonium or other reduced form of N are halogenated nitrophenols, hydrazine salts, o- and m-nitroanilines, dicyandiamide, several bromo or chloro substituted anilines (Alexander, 1977), and others such as thiourea (Quastel and Scholefield, 1949). N-Serve or 2 chloro-6-(trichloromethyl)-pyridine is considered the most promising (Reddy and Prasad, 1975). Inhibitors eliminate nitrification by inhibiting partially or completely the activity of *Nitrosomonas* and *Nitrobacter* (Campbell and Aleem, 1965; Shattuck and Alexander, 1963). Also, nitrification inhibitors have been found to reduce

overwinter losses of fall applied $\text{NH}_4\text{-N}$ in England (Gasser, 1965) and in the United States (Huber et al., 1969; Huber and Watson, 1972).

Some fall N fertilization in Alberta is done with urea. Urea is hydrolyzed to carbon dioxide and ammonia by the enzyme urease which is the trivial name for enzymes with the systematic name of urea amidohydrolase and refers to hydrolases which act on C-N bonds (nonpeptides) in linear amides (Bremner and Mulvaney, 1978). Denitrification losses from applied urea can be reduced by retarding the hydrolysis of urea after its application to soils.

Compounds that are inhibitors of the enzyme can be either inorganic or organic. Urea derivatives, such as thiourea, have been shown to be strong urease inhibitors (Kistiakowsky and Shaw, 1953; Malhi and Nyborg, 1979a).

Other compounds such as dithiocarbamates, boron containing compounds, formaldehyde, salts of heavy metals having atomic weights > 50 , quinone, polyhydric phenols and others, have been patented as inhibitors of urea hydrolysis in soil (Bremner and Mulvaney, 1978).

2.2.2 Use of different fertilizer management practices

2.2.2.1 Time of N fertilization

Autumn applications of N have been found inferior to equivalent spring applications at Rothamsted (Devine and Holmes, 1964), in north central Georgia (Olson et al., 1964) and in Ukraine (Dmitrenko et al., 1977). Stevenson and

Baldwin (1969), in experiments conducted in Ontario, showed that spring applications of ammonium nitrate, urea and anhydrous ammonia produced about 18% more corn grain than fall application of these fertilizers.

McAllister (1969), summarized 22 field trials conducted in the Prairie Provinces and reported that at 15 of 22 locations there were no differences in the yields of cereal grains between fall and spring N application. At three locations, fall application was better than spring application, and at four locations, spring applied N was better than fall applied N.

However, research conducted in the early 1970's frequently showed crop yield and N uptake to be favored by spring application. In several central Alberta studies, N uptake with spring application was about two times greater than with fall applied N (Leitch and Nyborg, 1972; Malhi and Nyborg, 1974). Field studies conducted in Manitoba (Partridge and Ridley, 1974) and in Saskatchewan (Paul and Rennie, 1977) suggested that fall applied N was often less efficient than spring application.

Also, the time of N application in the fall has proven to affect its nitrification during winter in areas of cold weather. The later the N was applied to the soil in fall, the slower was the rate of nitrification of the fertilizer N during winter (Malhi, 1978).

2.2.2.2 Concentrated forms of N fertilizers

Banding N fertilizers results in a high local concentration of ammonia and soluble salts. Gasser (1965), and Leitch (1973), found that band placement of ammonium sulfate reduced nitrification. The total amount of nitrate formed per unit area decreased with increased local concentration of NH_4 in the band (Wetselaar et al., 1972) and maximum nitrification in the band occurs near the edges of the diffused zone (Pang et al., 1973).

In flooded soils, the efficiency of applied N is sometimes considerably improved if fertilizer is placed in the reduced layer (Mitsui 1955; Broadbent and Mikkelsen, 1968). The application of ball-type fertilizer into the reduced layer is one of the most effective methods of decreasing nitrogen losses (Shiga et al., 1977). Many experiments indicate that ball type fertilizers made from mud soil or obtained from the market, increased both the N recovery by rice plants and grain yield, as compared to N fertilizers incorporated into the soil (Mitsui, 1955). Nitrogen release patterns from deep placement of urea appear to be a diffusion controlled process (Savant and De Datta, 1979). Nommik (1956), reported that gaseous loss from urea applied in pellets to a forest soil, was reduced significantly compared to broadcasting. He attributed this effect to a decrease in the rate of hydrolysis by increasing the pellet size. Baratemes and Morales (1977), in experiments with *Pinus* and *Eucalyptus* spp., reported that

fertilizers applied in pellets will release their nutrients slowly over a period of three years. Application of phosphorous fertilizer "in hole" may be beneficial for tomato production in southwestern Nigeria (Sobulo et al., 1978).

In recent years attempts have been made to develop compounds that release nitrogen slowly. Fertilizers such as sulphur-coated urea (SCU) and isobutylidene diurea (IBDU) have shown considerable potential as slow release materials (Frye, 1977; Islam and Parsons, 1979).

The previous description points out that there are diverse methods which can be used to control N losses, and with these methods it may be possible to overcome or minimize N losses occurring during the spring thaw in Alberta.

3. MATERIALS AND METHODS

3.1 Field experiments

3.1.1 Soils

Field experiments were conducted at three different sites, in the districts of Breton, Westlock and Bon Accord, in 1977-78. The description and location of the soils are in Table 1 and Figure 1, respectively.

3.1.2 Fertilizer treatment

In every experiment, all treatments except the control received a complete N,P,K,S fertilization. Nitrogen was applied as urea, ammonium sulfate or calcium nitrate at a rate of 56 kg N/ha. Phosphorous, potassium and sulfur were added at a rate of 41 kg P, 41 kg K and 17 kg S/ha as treble superphosphate and K_2SO_4 incorporated into the soil in the spring 1978. These rates were determined based on soil test.

Nitrogen fertilizers which were mixed, were first spread by hand on the soil surface and then worked into the soil approximately 10 cm deep with a "rototiller". Nitrogen fertilizers which were banded, were placed 5 cm deep in rows spaced at 30 cm or 60 cm. Nitrogen fertilizers which were nested, were placed 5 cm deep in a constricted hole (2 cm diameter), which were spaced at 30 cm x 30 cm or 60 cm x 60 cm. At the time of seeding in the spring, all treatments were rototilled in order to prepare the seed bed, and consequently the fall banded and nested N fertilizers no

Table 1. Some soil properties of the sites where field trials were established in the fall 1977.

Soil	Site	Depth	C	N	Moisture	
		(cm)	(%)	(%)	pH	1/3 bar
Luvisolic (Breton L)	1	0-15	1.3	0.18	6.44	24.9
		15-30	0.9	0.08	6.36	
Chernozemic (Falun L)	2	0-15	4.3	0.33	6.59	29.7
		15-30	3.0	0.30	6.60	
Chernozemic (Angus Ridge)	3	0-15	8.7	0.79	7.22	35.3
		15-30	5.9	0.63	7.29	

Moisture= Water retained by soil particles at 1/3 bar moisture tension. Values are expressed as percentage of oven dry weight of soils.

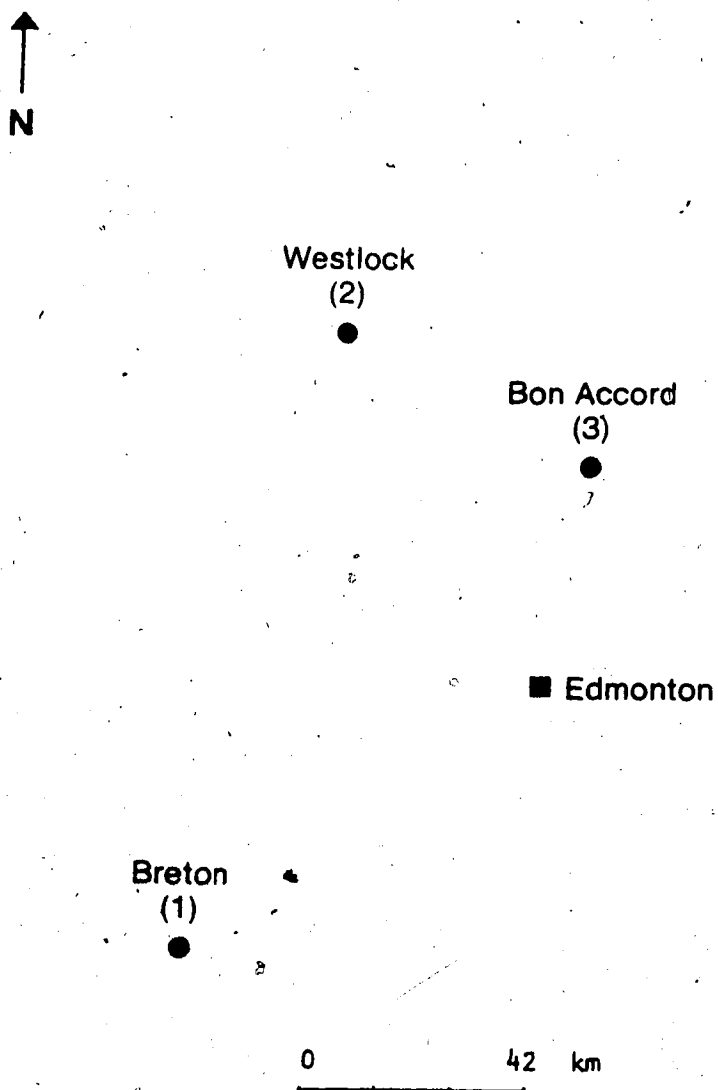


Figure 1. The location of the three field trials.

longer remained in bands or nests.

All plots were sown to barley (*Hordeum vulgare*, cult. 'Galt'), at a rate of 100 kg/ha, with a tractor-drawn plot seeder at the beginning of June, 1978. Weeds were removed by hand. Separation between rows was 22 cm and rows were N/S oriented and run parallel to fertilizer bands. Contiguous individual plots were 6.8 m long and 1.8 m wide. Thermistors were set up at each location in order to monitor soil temperature.

3.1.3 Experimental design

The following 14 treatments were established at each site, with each treatment replicated four times:

October 7 - 10

Control

Urea, mixed

Urea, nested (60 cm x 60 cm)

October 22 - 25

Calcium nitrate, mixed

Urea, mixed

Urea, banded (30 cm)

Urea, banded (60 cm)

Urea, nested (30 cm x 30 cm)

Urea, nested (60 cm x 60 cm)

Ammonium sulfate, mixed

Ammonium sulfate, nested (60 cm x 60 cm)

November 3 - 6

Urea, mixed

Urea, nested (60 cm x 60 cm)

June 1 - 4, 1978

Urea, mixed

The data for each site were analyzed using a randomized complete block design. Blocks were set up based on the land slope. Duncan's multiple range test was conducted for significant differences among treatments.

Although the factorial nature of the above treatments suggests a split-plot design may be appropriate, a completely randomized block design was selected for the following reasons:

a. This study was part of a project in which similar tests are and have been treated as randomized complete block design (Malhi, 1978; Malhi and Nyborg, 1979). Also, the field plot design was prepared when this part of the project started.

b. It is possible with designs such as the one used here that error variance may not be homogeneous. Treatments were divided into subgroups, (time of application), and analysis of variance was conducted. The difference between error variance of the subgroups was not statistically significant according to both, the Burr-Foster (Q-test), and the Bartlett test. Therefore, the overall error variance was considered to be a fair estimate of each subdivided unit. Consequently, it was felt that analysis as a randomized complete block design was legitimate.

c. The main objective of the experiment was to test the capacity of N fertilizers applied in the fall, and placed in nests, to increase the yield and N uptake by the barley crop as compared to other methods of application. Interactions between type of fertilizers and method of application, for example, were not primary objectives. In this context, according to Chew (1976), it is acceptable and valid to compare the 14 treatment combinations using Duncan's multiple range test. It is recognized that other variable interactions may be significant.

3.1.4 Soil sampling

In all field experiments, soil samples from the control and mixed treatments were taken from the following depths: 0 - 15 cm, 15 - 30 cm, 30 - 60 cm, 60 - 90 cm and 90 - 120 cm. Samplings was conducted prior to the application of fertilizer in October 1977 and after fertilization, when soils were frozen in November, January, March and after the spring thaw in April 1978. For the 0 - 15 cm depth, each soil sample consisted of nine cores per plot taken with a 3.8 cm diameter coring tube ("step sampler"). For the 15 - 30 cm depth, the sample consisted of seven cores taken with a 2 cm diameter coring tube ("Oakfield" sampler). Below the 30 cm depth, four cores of a 2.4 cm diameter were taken with a hydraulic truck-mounted sampler. For every depth, the cores were combined.

The plots where N fertilizers were applied in fall and placed in bands or in nests, were sampled with different techniques. Where bands were spaced at 30 cm, two subsamples were taken per replicate. The first, consisting of a cubic volume of soil 15 cm x 15 cm x 15 cm, was dug with a chisel across the band; the second subsample taken beside the band, had dimensions of 7.5 cm (perpendicular to the band) x 15 cm (parallel to the band) x 15 cm (deep), so that diffusion of N fertilizer between two rows could be measured. When bands were spaced at 60 cm, a cubic volume of soil 15 cm x 15 cm x 15 cm was dug from across the band. The dimensions of the second subsample were 23 cm (long) x 15 cm (wide) x 15 cm (deep).

Nest treatments were sampled using the dimensions already described for band sampling. A sample containing the nesting zone of 15 cm x 15 cm x 15 cm was dug. The lateral samples of nests located at 30 cm x 30 cm and 60 cm x 60 cm, were taken in a manner identical to that used for the respective band distances.

Prior to seeding all the plots were rototilled and soil samples were taken the same way as described for the control and mix treatments. Soil samples were air dried, passed through a 2 mm sieve and analyzed for urea-N, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ content.

3.1.5 Grain and straw sampling

The samples of barley plants, cut at ground surface, consisted of 5 m from each of the central two rows of each treatment. The samples were placed in cloth sacks, oven-dried at 65 C for seven days, weighed and threshed to determine the grain yield. Representative grain and straw samples were collected, ground to 40 mesh and analyzed for total N.

3.2 Incubation experiments

Soil samples of the Ap horizons, which were low in mineral N content, were taken from two of the three sites, air dried and passed through a 2 mm sieve before incubation. The incubation experiments were conducted under controlled conditions of temperature (24 C) and moisture (1/3 bar). Urea was either placed in a nest (1.16 g urea per pot or per box) or mixed into the soil (31.4 ug N/g soil). These two rates were equivalent to 56 kg N/ha/0.15 m depth.

3.2.1 Pot and box incubation experiments

Samples of both soils were weighed into plastic pots to provide 500 g, 1000 g, 2000 g and 4000 g of soil. Different pot sizes were used to study possible effects of the volume on nitrification and diffusion of urea from the nesting zone. The soils were preincubated for one week prior to the application of urea. After adding urea, the pots were closed with plastic having holes 3 mm in diameter to allow

aeration. The containers were set out in a randomized complete block design with three replicates for each sampling period.

Samples consisting of different concentric sections of soil were taken from each pot where urea was placed in a nest. Moist soil samples were analyzed for urea-N, $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ each 8 days for a period of 24 days. Incubations of soil samples with urea placed in nests were also made in wooden boxes with dimensions of 30 cm x 30 cm x 15 cm (deep).

Duplicate samples of only the Black Chernozemic soil were incubated with urea placed in nests. From each box, three different sections of soil were obtained, (sections a, b, c of Figure 3). Determinations of *Nitrosomonas*, *Nitrobacter*, pH, E.C., and $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$, were also made for every soil section at each sampling. The same determinations were conducted on Black Chernozemic soil samples where urea was mixed into the soil.

3.2.2 Urease assay

Samples of the Ap horizon of the Luvisolic and the Chernozemic soils were incubated with five different concentrations of urea (5 mM, 10 mM, 20 mM, 40mM and 80 mM in solution) at five different soil temperatures (-5 C, 0 C, 10 C, 20 C and 30 C). The incubation of soil samples to measure urease activity at subzero temperatures was made following the method described by Bremner and Zantua,

(1975). The assays for urease were conducted based on the method described by Tabatabai and Bremner (1972), with the exception that the disappearance of substrate (urea) rather than the appearance of product (NH_4), was measured.

3.3 Analytical procedures

Ammonium, nitrite, nitrate and urea were extracted from soil samples by shaking 10 g of soil with 100 ml 2M KCl-PMA solution for one hour (Douglas and Bremner, 1972). Determinations of NH_4 , NO_2 , NO_3 were made by steam distillation (Bremner, 1965a). Urea was determined from the same extract using the colorimetric method described by Douglas and Bremner (1972).

Total N was measured by the semimicro-Kjeldahl method (Bremner, 1965b) and total soil organic carbon was determined by dry combustion in the Leco furnace (Tabatabai and Bremner, 1970). Soil pH was measured with a pH meter using a glass electrode in a suspension of 1:2.5, soil:water ratio.

The particle size analysis of soil samples was carried out by the hydrometer method (Bouyoucos, 1962). The moisture content of soils at 1/3 bar tension was determined by the porous plate method as described in the USDA Handbook 60, (United States Salinity Laboratory Staff, 1954). The procedure to measure electrical conductivity was taken from the same Handbook 60, (1954). Bulk density was determined by

taking two field cores at each site from the 0-15 cm, 15-30 cm, 30-60 cm, 90-120 cm depth.

The bacterial population of *Nitrosomonas* and *Nitrobacter* was estimated by the MPN procedure described by Alexander and Clark, (1965). Km values were calculated using the Lineweaver-Burke plot (Bull, 1971).

4. RESULTS

4.1 Mineralization of the native soil N during winter

One of the objectives of the field trials established in the fall, was to measure some transformations of soil and fertilizer N during winter when soils were frozen.

The initial inorganic N content of the soils in October 1977 at the three sites is shown in Figure 2.

At Breton, (site 1), 12 kg of mineral-N/ha was present in the top 30 cm of soil in October and it increased constantly to 38 kg mineral-N/ha in March, and 37% of this mineral-N accumulated as NO_3 . The mineral-N content decreased in April to 24 kg N/ha. This represented a loss of 35% of the mineral-N which was present in March (Figure 2).

At Westlock, (site 2), the soil mineral-N in the top 30 cm of soil increased from 20 kg N/ha in October to 60 kg N/ha in March, with 55% of this N present as NO_3 . By April, the mineral-N decreased to 31 kg/ha, representing a loss of 49% of mineral-N present in March (Figure 2).

At Bon Accord, (site 3), the mineral-N in the top 30 cm of soil increased from 11 kg N/ha in October to 85 kg N/ha in March with 57% of this N present as NO_3 . By May, 35% of the mineral-N found in March had disappeared from the first 30 cm of soil.

In summary, it was found that mineralization and nitrification of the soil N occurred during winter in frozen soils and that much of the mineralized N was lost during the

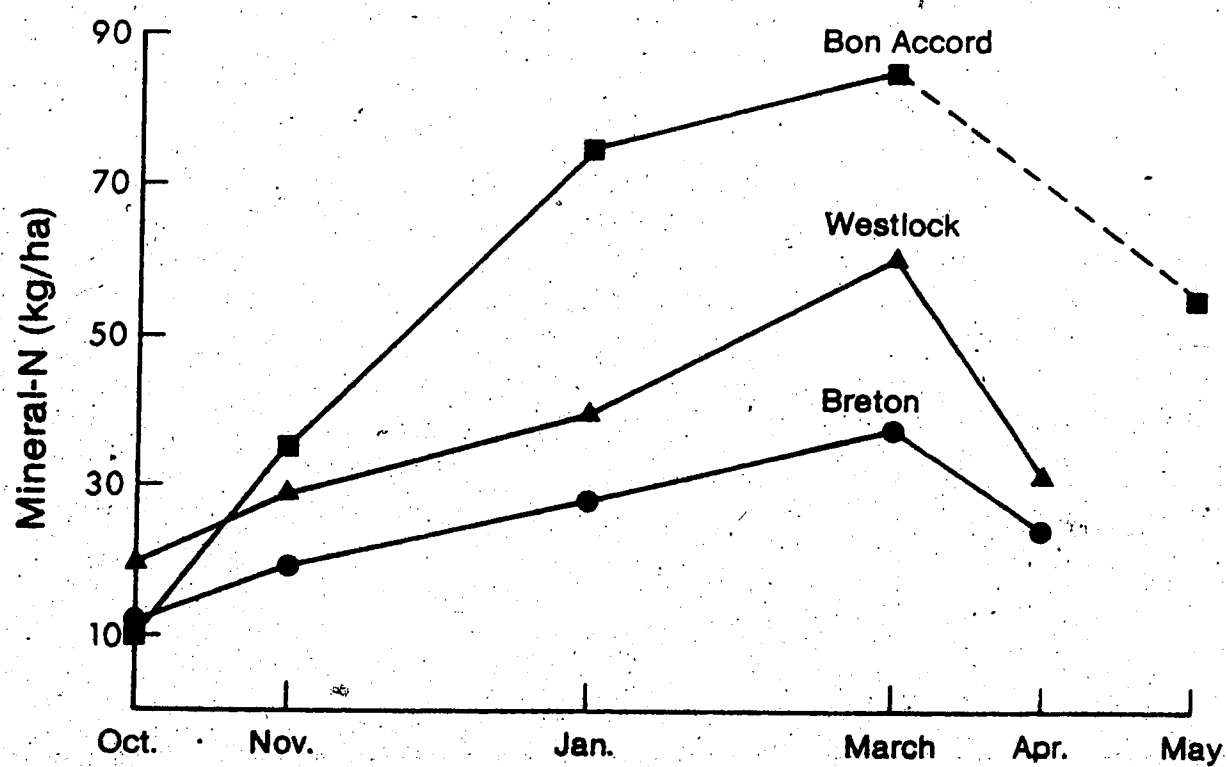


Figure 2. Mineralization of the soil nitrogen (in 0-30 cm) from fall to spring at the three sites of experimentation.

spring thaw (see Appendix Tables 1 to 12).

4.2 Recovery of fall applied N fertilizer

Soil sampling conducted in November, January, March, April and May, indicated a higher recovery of the urea-N when it was placed in nests than when it was banded or mixed into the soil. Table 2, shows that the recovery of nest applied N fertilizer, at the three sites, was never less than 77% and in one case was as high as 98%. The apparent recovery of fertilizer-N as mineral-N, $[(\text{Mineral-N in fertilized treatment} - \text{Mineral-N in control})/56] \times 100$, across sites and including different times of application, ranged from 56% to 91% being very variable among the different sites. The recovery of fall applied urea-N, mixed into the soil was dependent on the time of application. The later it was applied in the fall, the higher was the recovery of the urea-N.

4.3 Nitrification, immobilization and other transformations of urea placed in nests and mixed into the soil

The nitrification rate of urea, $[(\text{NO}_3\text{-N in fertilized treatment} - \text{NO}_3\text{-N in control})/56] \times 100$ applied in early October and placed in nests, was extremely slow at all sites (Table 3). By March no nitrification of urea had occurred at site 2, and only 6 and 4% of the urea was nitrified at sites 1 and 3, respectively. On the other hand, nitrification of

Table 2. The recovery of urea as mineral-N ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) at different times, after urea was applied in fall 1977, at a rate of 56 kg N/ha at the three sites.

<i>Recovery of urea as mineral-N (%)</i>					
Site	Treatment	Nov.	Jan.	March	April or May
1	7-10 Oct.				
	Mix	69c *	76c	72b	59b
	Nest	98a		90a	77a
	22-25 Oct.				
	Mix	78b		88a	78a
	Band	80b	83b		79a
2	3-6 Nov.				
	Mix		89a	88a	78a
	7-10 Oct.				
	Mix	79c	75c	78d	56c
	Nest	94a	86a	91a	86a
	22-25 Oct.				
3	Mix	81c		81bc	76b
	Band	88b		86ab	78b
	3-6 Nov.				
	Mix		82a	82bc	88a
	7-10 Oct.				
	Mix	75c	74c	73b	56d
	Nest	98a	81b	83a	95a
	22-25 Oct.				
	Mix	80bc		84a	76c
	Band	82b	75c		82b
	3-6 Nov.				
	Mix		88a	88a	91a

* Within columns and for each site, values not followed by the same letter are significantly different from each other ($p=0.05$).

the urea applied in early October and mixed into the soil was equal to 29%, 53% and 76% at sites 1, 2 and 3, respectively. By March, nitrification of the urea applied late in autumn and mixed into the soil, was 16%, 20% and 39% at sites 1, 2 and 3, respectively (Table 3).

An experiment was carried out in the laboratory to test the hypothesis that urea mixed into the soil and placed in nests, is nitrified at different rates, and further that the method of N placement would affect immobilization upon addition of barley straw to soil samples.

Table 4, indicates that only 4%, 17% and 36% of recovered urea placed in nests was present as nitrate, $[(\text{NO}_3\text{-N in fertilized treatment} - \text{NO}_3\text{-N in control})/56] \times 100$, after 8, 16 and 24 days of incubation respectively, in the Gray Luvisolic soil sample. In comparison, 73%, 73% and 82% of the recovered urea mixed into the soil was present as nitrate after 8, 16 and 24 days, respectively. Nitrification rates for the Black Chernozemic soil sample are reported in the same Table. Urea placed in nests, also decreased the rate of nitrification in this soil and 33%, 29% and 30% of the urea accumulated as nitrate after 8, 16 and 24 days, respectively. When urea was mixed into the soil, nitrification was almost complete (91%) during the first eight days of incubation. After 24 days, 97% of the mineral nitrogen was nitrified.

The recovery of urea as mineral-N, in the Luvisolic soil sample, where urea was placed in nests, was increased

Table 3. The recovery in March of NO₃-N to a depth of 120 cm, from fall applied urea-N at a rate of 56 kg N/ha.

Method of application	Time of application	Recovery of urea as NO ₃ -N (kg/ha)		
		Site 1	Site 2	Site 3
Mix	7-10 Oct.	*16.0c	30.0c	42.6c
Nest	7-10 Oct.	3.2a	0.0a	2.1a
Mix	23-26 Nov.	9.0b	11.2b	21.8b

* Within columns, values not followed by the same letter are significantly different from each other (p=0.05)

Table 4. The recovery of urea as $\text{NO}_3\text{-N}$ after it was placed in nests and mixed into the soil. Soil samples were incubated in wooden boxes (nested) and in pots (mixed) at 1/3 bar moisture and at 24 C. Urea was applied at a rate of 1.16 g/box and 31.4 ug N/g soil in each pot.

Soil	Method of application	Net recovery of urea as $\text{NO}_3\text{-N}$ (ug N/g soil) after days of incubation		
		8	16	24
Gray Luvisolic	Nest	*1.1a	5.4a	11.2a
	Mix	22.9b	22.8b	26.0b
Black Chernozemic	Nest	10.3a	9.1a	9.4a
	Mix	21.4b	21.5b	23.0b

* Within columns and for each soil, values not followed by the same letter are significantly different from each other ($p=0.05$).

compared to the mixed treatment and was almost independent of the addition of straw (Table 5). When straw was not added to soil samples, the recovery of N added as urea and placed in nests was 101% and 99%, after 8 and 24 days of incubation, respectively. At the same time, the recovery of N applied as urea and mixed into the soil was 83% and 82%, respectively. However, when straw was added at a rate of 4 t/ha, the recovery of N applied as urea mixed into the soil was only 6% and -13% after 8 and 24 days, respectively. The recovery of N applied as urea and placed in nests, was 101% and 70% after 8 and 24 days of incubation, respectively (Table 5). Black Chernozemic soil samples also showed

Table 5. The recovery of urea as mineral-N ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$) after it was placed in nests and mixed into the soil. Soil samples were incubated at 1/3 bar moisture and at 24 C. Urea applied at a rate of 56 kg N/ha.

Soil	Addition of straw (t/ha)	Method of application	Recovery of urea as mineral-N (%), after days of incubation		
			8	16	24
Gray Luvisolic	0	Mix	*83b	78b	82b
	0	Nest	101a	97a	99a
	4	Mix	6c	-15c	-13d
	4	Nest	101a	99a	70c
Black Chernozemic	0	Mix	70b	72b	60b
	0	Nest	102a	94a	94a
	4	Mix	-27c	-11d	-7d
	4	Nest	98a	43c	46c

* Within columns and for each soil, values not followed by the same letter are significantly different from each other ($p=0.05$).

similar differences of N immobilization when urea was placed in nests or mixed into the soil, but there were differences in the magnitude of the N recovered from the applied urea (Table 5).

In summary, nest placement of urea slowed its nitrification and prevented, to a large extent, immobilization of the applied N, after straw was added to the soil.

4.3.1 Variation of the nitrifying population as caused by method of urea placement.

Since nitrification of urea placed in nests was inhibited under field and laboratory conditions, MPN (most probable number) determination of *Nitrosomonas* and *Nitrobacter* were made to test the hypothesis that nest placement of urea affects the growth and/or activity of these autotrophs.

Table 6, shows the variations in the nitrifying population after urea was placed in a nest or mixed into the soil. At time zero, the initial counting gave 24,000 cells of *Nitrosomonas* cm^{-3} and only 1,400 *Nitrobacter* cells cm^{-3} of soil. In the control soil samples, without urea, the number of *Nitrobacter* cells increased to 29,000 cells cm^{-3} after eight days of incubation. The population of *Nitrosomonas* and *Nitrobacter* remained unchanged at 29,000 cells cm^{-3} of soil until the incubation was terminated on the 24th day.

Mixing urea into the soil, resulted in an explosive growth of *Nitrobacter*. The population increased to 770,000 cells cm^{-3} soil and 6,800,000 cells cm^{-3} soil after 8 and 16 days of incubation, respectively. After 24 days the number of *Nitrobacter* cells dropped to 100,000 cm^{-3} of soil.

Nitrosomonas, whose population remained constant during the first sixteen days of incubation, dropped from 29,000 cells to 16,000 cells cm^{-3} of soil after 24 days of incubation (Table 6).

Urea placed in nests, inhibited the growth of *Nitrobacter* during the first eight days of incubation (Table 6). After 16 days, only a slight increase of these autotrophs was observed. After 24 days, their number was increased to 100,000 cells cm^{-3} of soil.

Variations in the population of *Nitrosomonas* and *Nitrobacter* occurred depending first, on their location with respect to the nesting zone and second, on the time of incubation. Figure 4, shows the distribution of these autotrophs in space and time.

The central section of soil, including the nesting zone, (section a), showed an extraordinary growth of *Nitrosomonas* after 8 days, but after 16 and 24 days, the number of cells dropped to 620,000 cells cm^{-3} soil and 158,000 cells cm^{-3} . In this same section of soil, the number of *Nitrobacter* cells remained unchanged during the first 8 days of incubation. After 16 and 24 days, the population of *Nitrobacter* grew to 29,000 cells cm^{-3} and

Table 6. Variation of the nitrifying population in a Black Chernozemic soil incubated with urea placed in nests and mixed into the soil. Soil samples were incubated at 24 °C and at 1/3 bar moisture. Urea was applied at a rate of 56 kg N/ha.

Method of application	Nitrifying organism	MPN (cells x cm ⁻³ of soil x 10 ³) after days of incubation.			
		0	8	16	24
Control	Nitrosomonas	24.0	* 29.0b	29.0b	29.0a
	Nitrobacter	1.4	29.0b	29.0b	29.0a
Mix	Nitrosomonas		24.0b	24.0b	16.0a
	Nitrobacter		770.0d	6,800.0d	100.0b
Nest	Nitrosomonas		105.0c	750.0c	37.2a
	Nitrobacter		1.4a	2.0a	100.0b

* Statistical analysis was conducted with the log of the number of cells. Within columns, values not followed by the same letter are significantly different from each other (p=0.05).

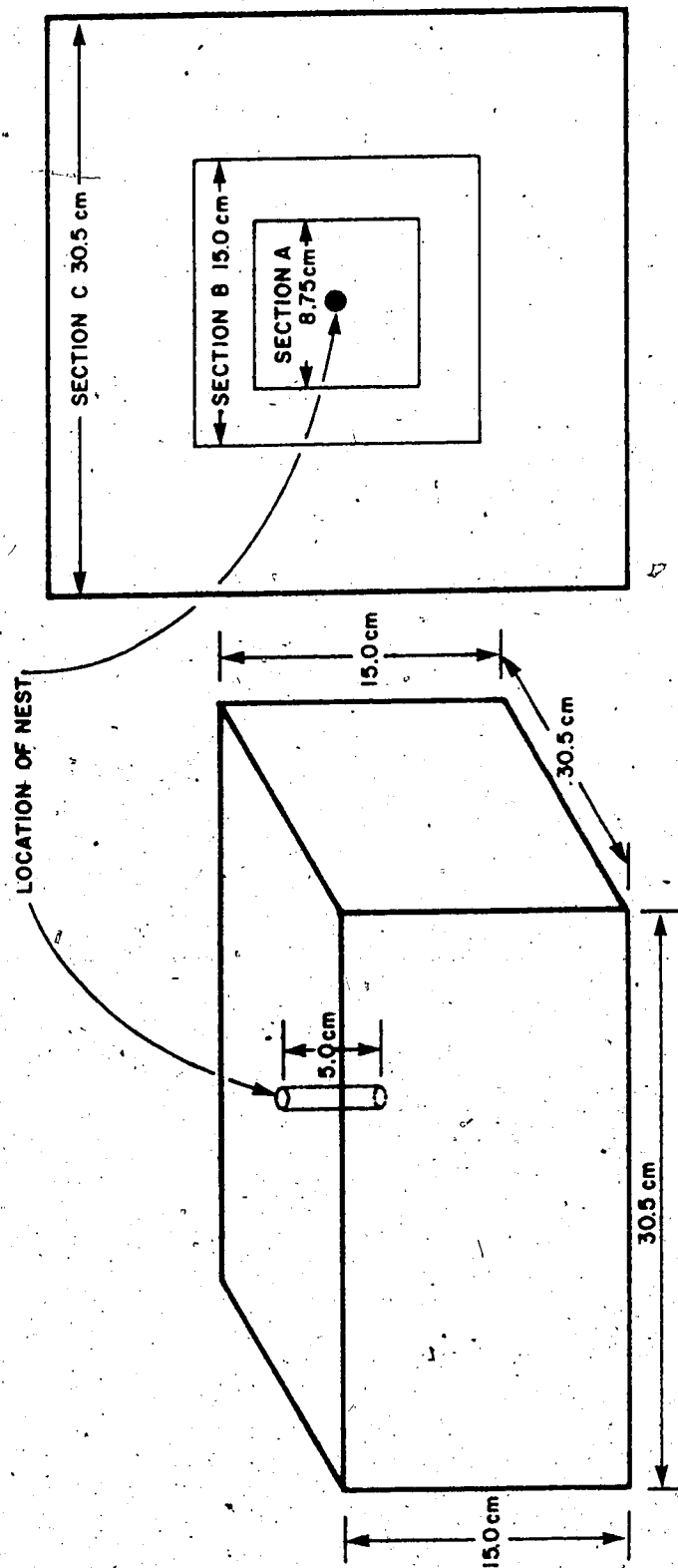


FIGURE 3. SOIL SAMPLES INVOLVING SECTIONS A, B AND C OF A WOOD BOX WHERE UREA WAS PLACED IN NESTS AND INCUBATED AT 24° C AND AT 1/3 BAR MOISTURE.

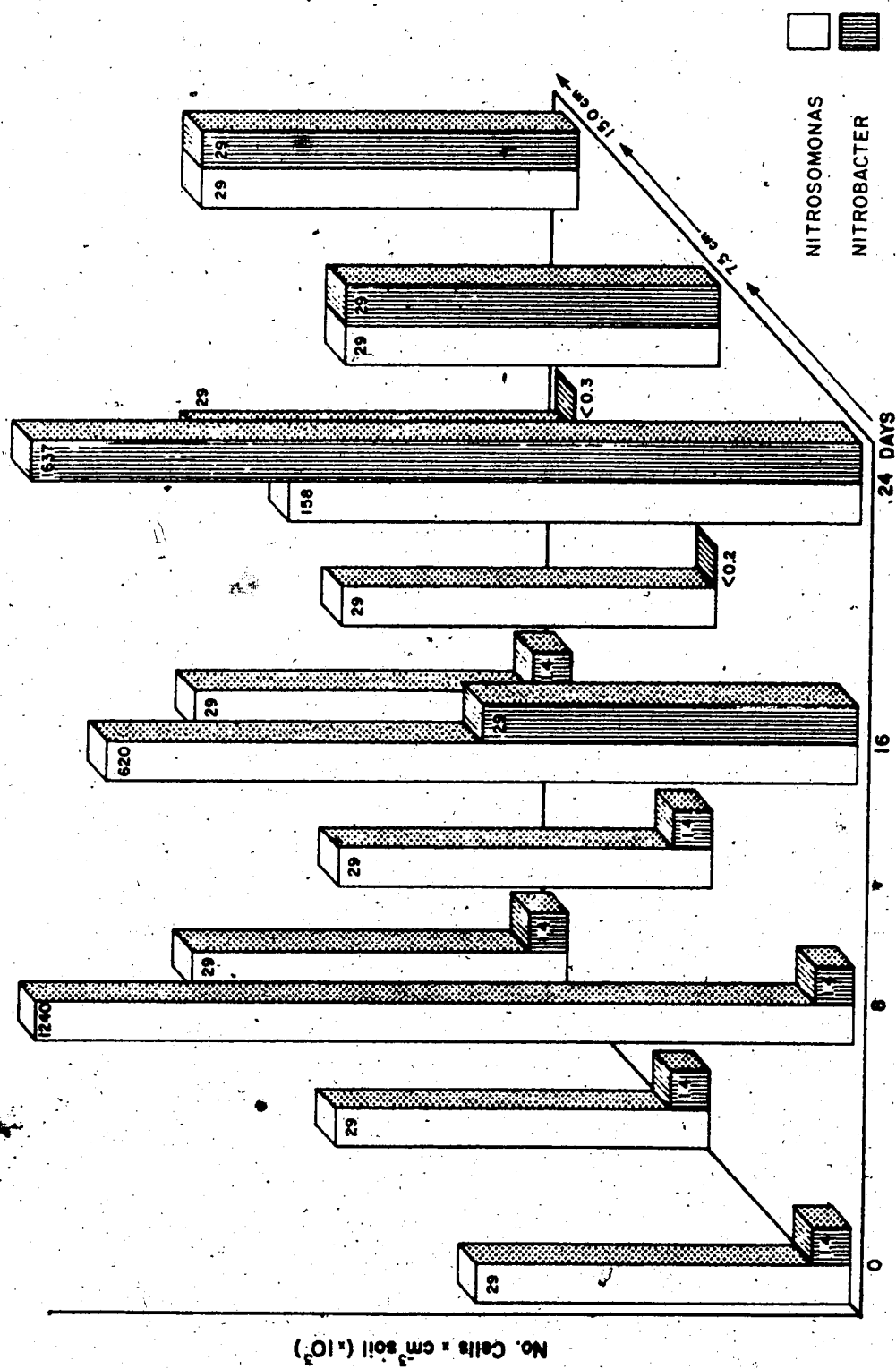


FIGURE 4. VARIATION OF NITROSOMONAS AND NITROBACTER IN A CHERNOZEMIC SOIL, AS INDUCED BY UREA PLACED IN NEST.

1,600,000 cells cm^{-3} , respectively.

No changes in the population of *Nitrosomonas* were produced in sections b and c of Figure 3, during the rest of the incubation period. However, the *Nitrobacter* population varied in these two external sections of soil. Between the eighth and the sixteenth day of incubation, its population was reduced to less than 100 cells cm^{-3} of soil soil and to less than 300 cells cm^{-3} in soil sections b and c, respectively. Although, the population of *Nitrobacter* in both sections increased to 29,000 cells cm^{-3} soil, after 24 days of incubation, it was not larger than that in the control soil.

In summary, *Nitrosomonas* and especially *Nitrobacter* were affected by placing the urea in nests. *Nitrobacter* cells did not grow during the first 16 days of incubation. On the other hand, when urea was mixed into the soil, the growth of *Nitrobacter* was greatly enhanced. In the control soil, the population of *Nitrobacter* and *Nitrosomonas* did not change after the eighth day of incubation.

4.3.2 Variation of E.C. and pH caused by method of urea placement.

Determinations of E.C. and pH were used to determine if changes in these two properties were associated with variations produced in the population of the nitrifying bacteria (Table 7a, 7b).

Table 7a. Variation of the soil electrical conductivity (E.C.) and soil pH, produced by urea placed in nests and mixed into the soil. Urea applied at a rate of 56 kg N/ha. Soil samples incubated at 24 C and at 1/3 bar moisture.

<i>Variation of the soil electrical conductivity (E.C.) and pH after days of incubation.</i>						
Treatment	8		16		24	
	E.C.	pH	E.C.	pH	E.C.	pH
Control	0.8	6.54	0.8	6.50	0.7	6.45
Mix	1.5	6.75	2.4	6.20	3.6	6.66
Nest *						
(a)	13.6	7.02	14.4	7.08	14.4	7.10
(b)	0.9	6.62	5.3	6.74	2.4	6.96
(c)	0.8	6.62	0.8	6.20	1.8	6.10

* See Figure 3.

Table 7b. Variation of pH in soil samples (0-15 cm) taken from the field trials after urea was applied in the fall at a rate of 56 kg N/ha.

	Time of applica- Site tion	Treatment	Nov.	Jan.	March	April
1	7-10 Oc.	Nil	6.40	6.25	6.50	6.49
		Mix	6.33	6.29	6.41	6.35
		Nest (a)*	7.15		6.92	6.97
		Nest (b)*	6.61		6.24	6.39
	22-25 Oct.	Mix	6.50		6.45	6.45
		Band (a)*	6.37	6.35		6.34
		Band (b)*	6.37	6.29		6.25
	3-6 Nov.	Mix		6.19	6.37	6.30
2	7-10 Oct.	Nil	6.56	6.48	6.65	6.76
		Mix	6.58	6.55	6.68	6.87
		Nest (a)	7.33	6.94	6.98	6.89
		Nest (b)	6.76	6.56	6.56	6.59
	22-25 Oct.	Mix	6.69		6.70	6.71
		Band (a)	6.69		6.57	7.45
		Band (b)	6.67		6.52	6.62
	3-6 Nov.	Mix		6.53	6.56	6.66
3	7-10 Oct.	Nil	7.46	7.41		7.38
		Mix	7.64	7.41	7.38	
		Nest (a)	7.92	7.91	8.08	
		Nest (b)	7.88	7.54	7.56	
	22-25 Oct.	Mix	7.55		7.58	
		Band (a)	7.92	7.48		
		Band (b)	7.65	7.50		
	3-6 Nov.	Mix		7.60	7.46	

* a = zone involving the nesting or banding zone.

* b = zone immediately adjacent to the nesting or banding zone.

Soil samples that were used as control, gave fairly constant values of E.C. and pH throughout the incubation period.

Mixing urea into the soil, resulted in a moderate increase of pH during the first eight days of incubation. The pH increased from 6.53 to 6.78 and fluctuated between 6.20 and 6.66 after 16 and 24 days. The electrical conductivity (E.C) of the soil increased constantly from 1.45 mmhos/cm to 3.60 mmhos/cm between the eighth and the twenty fourth day of incubation.

Urea placed in nests produced the most dramatic changes in soil pH and E.C. values. This was especially pronounced in the cubic section of soil involving the nesting zone (section a, Figure 3). In this section of soil, the E.C. was unusually high at 13.6 mmhos/cm and remained almost constant until the end of the experiment. The pH of this soil section increased to 7.02, 7.08 and 7.10 after 8, 16 and 24 days of incubation, respectively.

Soil samples taken from the field experiments after the establishment of the plots during fall, showed that the pH of the soil section involving the nest zone was increased even more to values of 8.0 and higher (Table 7b). The pH in soil sections b and c, was similar or a little higher than the pH of the control samples. The same trend was observed with the pH of soil samples taken from the field trials (Table 7b). The electrical conductivity (E.C) for sections b and c, was lower than that shown by the area involving the

nesting zone (Table 7a)..

In general, urea placed in nests, caused an increase in the E.C. in the zone involving the nest. The pH values were also increased. These large variations in electrical conductivity, were not found in the external soil sections. Urea mixed into the soil, produced only minor variations in soil pH and electrical conductivity.

4.3.3 Transformation of urea into inorganic forms

The following experiment was carried out in the laboratory to determine the distribution and transformation of urea placed in nests as compared to urea mixed into the soil.

Figure 5 shows that urea placed in nests in a Luvisolic soil sample incubated in pots containing 500 g of soil, substantially reduced the rate of oxidation of the ammonium to nitrate as compared to mixing the urea into the soil. After five days of incubation, only 63% of the urea applied in nests was hydrolyzed. The recovered mineral-N showed that 57% of the hydrolyzed urea was as $\text{NH}_4\text{-N}$, 0.3% as $\text{NO}_2\text{-N}$ and 0.9% as $\text{NO}_3\text{-N}$. The NH_4/NO_3 ratio was 35. Urea mixed into the soil was hydrolyzed completely within 5 days and was nitrified at a much higher rate; 11% of the urea was found as ammonium-N and 82% accumulated as $\text{NO}_3\text{-N}$. The NH_4/NO_3 ratio was 0.11 and nitrite did not accumulate. After 10 days of incubation, the urea placed in nests was almost completely hydrolyzed and nitrate accumulated slightly. Only

1% of the applied urea accumulated as NO_2^- -N. The $\text{NH}_4^+/\text{NO}_3^-$ ratio decreased, but was still very high at 15.4.

After 15 days of incubation, the $\text{NH}_4^+/\text{NO}_3^-$ ratios were 0.08 and 6.1 in the mixed and nested treatments, respectively. At the end of the 25 days of incubation, 32% and 80% of the added urea was present as NO_3^- -N in the nest and mix treatments, respectively. The $\text{NH}_4^+/\text{NO}_3^-$ ratio was 2.4 as compared to 0.038 shown by the urea mixed into the soil.

Incubation of urea placed in nests, was also conducted in larger pots containing 1000 g, 2000 g and 4000 g of soil. Urea was applied at the same rate (1.16 g urea/pot). The dynamic of the urea hydrolysis and oxidation were quite similar to that shown in the 500 g pot. However, there were differences in magnitude, especially regarding the $\text{NH}_4^+/\text{NO}_3^-$ ratio. This ratio decreased with increasing pot size and with time of incubation (Appendix, Table 13).

The N recovery from different pot sizes and with urea placed in nests, was almost complete and ranged between 92% and 98% during the first fifteen days of incubation. When the incubation was terminated after 25 days, the recovery of the applied N had decreased to about 75%. On the other hand, the recovery of N after urea was mixed into the soil was 83%, 77% and 80%, after 5, 15 and 25 days of incubation, respectively.

An identical experiment was conducted with Black Chernozemic soil samples incubated with urea placed in nests in pots containing 500 g, 1000 g and 2000 g of soil. These

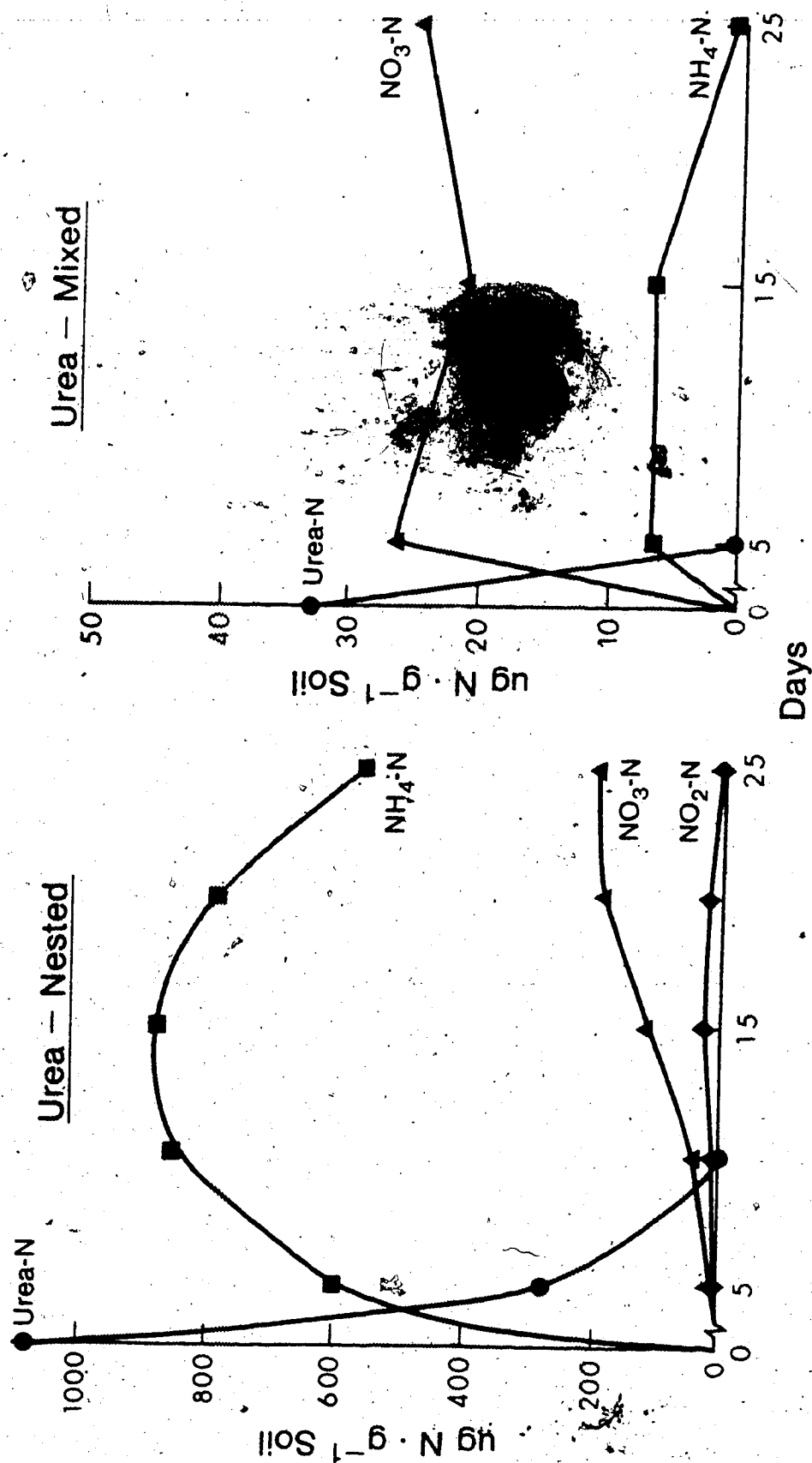


Figure 5. Transformation of urea into inorganic nitrogen forms. Urea was placed in a nest (1.16 g urea/pot) and mixed into the soil (31.4 $\mu\text{g N/g}$ soil). Luvisolic soil samples were incubated at 1/3 bar and at 24 °C.

results (Appendix, Table 14) also showed a reduction in the rate of urea hydrolysis and nitrification as compared to urea mixed into the soil.

4.3.4 Distribution of different N forms with respect to the nesting zone

Figure 6 shows the lateral distribution of urea, NH_4 , NO_2 , and NO_3 after 5, 15 and 25 days, in soil samples incubated with urea placed in nests. Soil samples were taken with 3 concentric cylinders, 2.2 cm, 5.4 cm or 8.6 cm in diameter and 10 cm high. The lateral distances of 0 cm, 2 cm and 4 cm are used to designate the distances existing between the central zone of application and the other two concentric cylindric sections (Figure 7). Vertical distribution will not be described since the concentration of the different inorganic N forms was quite similar above or below the zone of application in each of the concentric sections of soil.

Urea was placed in nests in the Luvisolic soil sample, at the center of the pot and 3 cm deep. After 5 days, the central soil section containing the nesting zone had concentrations of 40 and 130 $\mu\text{g N/g soil}$ as urea and ammonium respectively; contents of nitrite and nitrate were negligible. At approximately 2 cm from the zone of application, there was an increase in urea and ammonium contents to 300 and 360 $\mu\text{g N/g soil}$, respectively. Only 5 and 0.8 $\mu\text{g N/g soil}$ were found as nitrate and nitrite

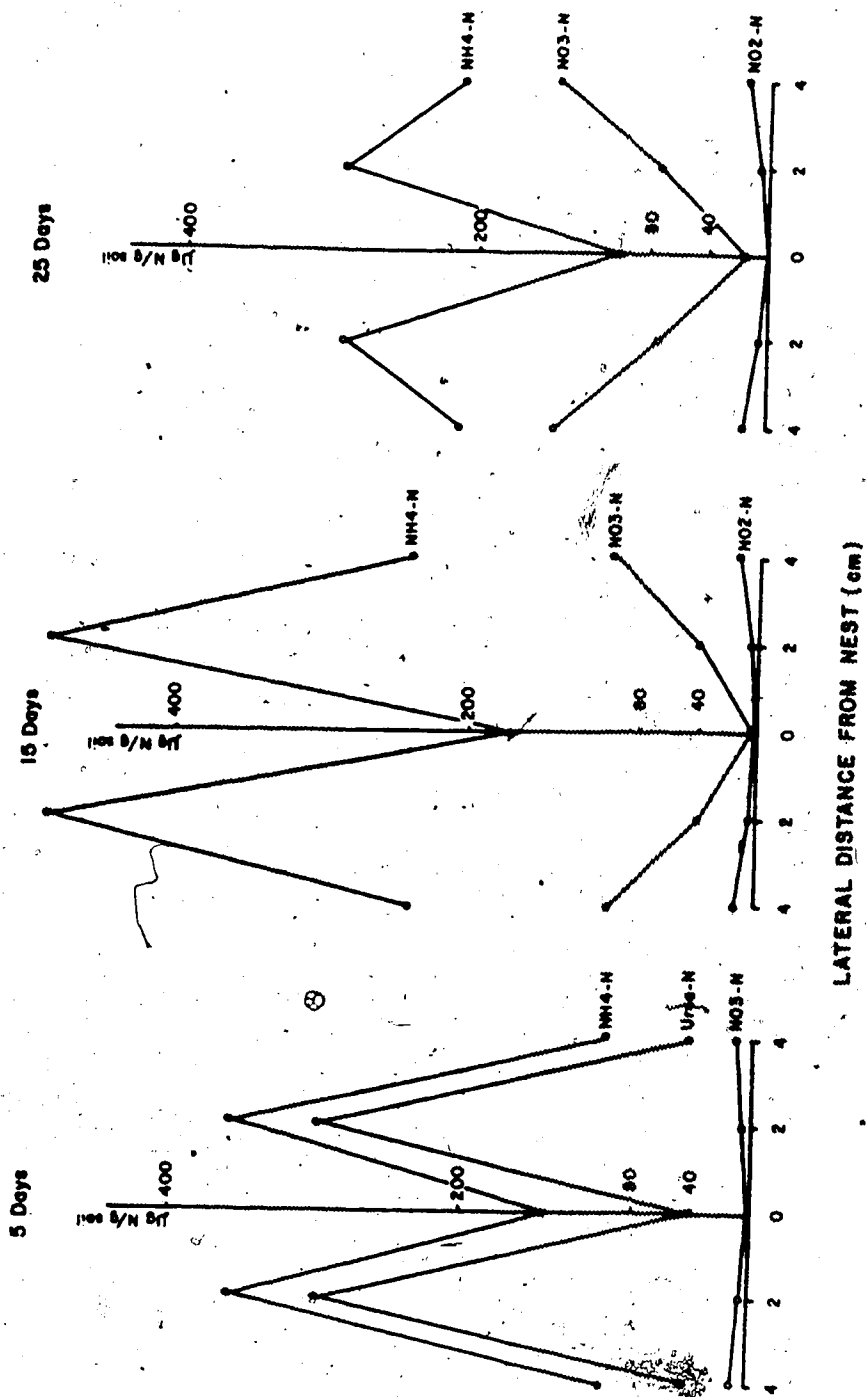


FIGURE 6. DISTRIBUTION OF DIFFERENT N FORMS RESPECT TO THE NESTING ZONE IN A POT CONTAINING 500 g OF SOIL.

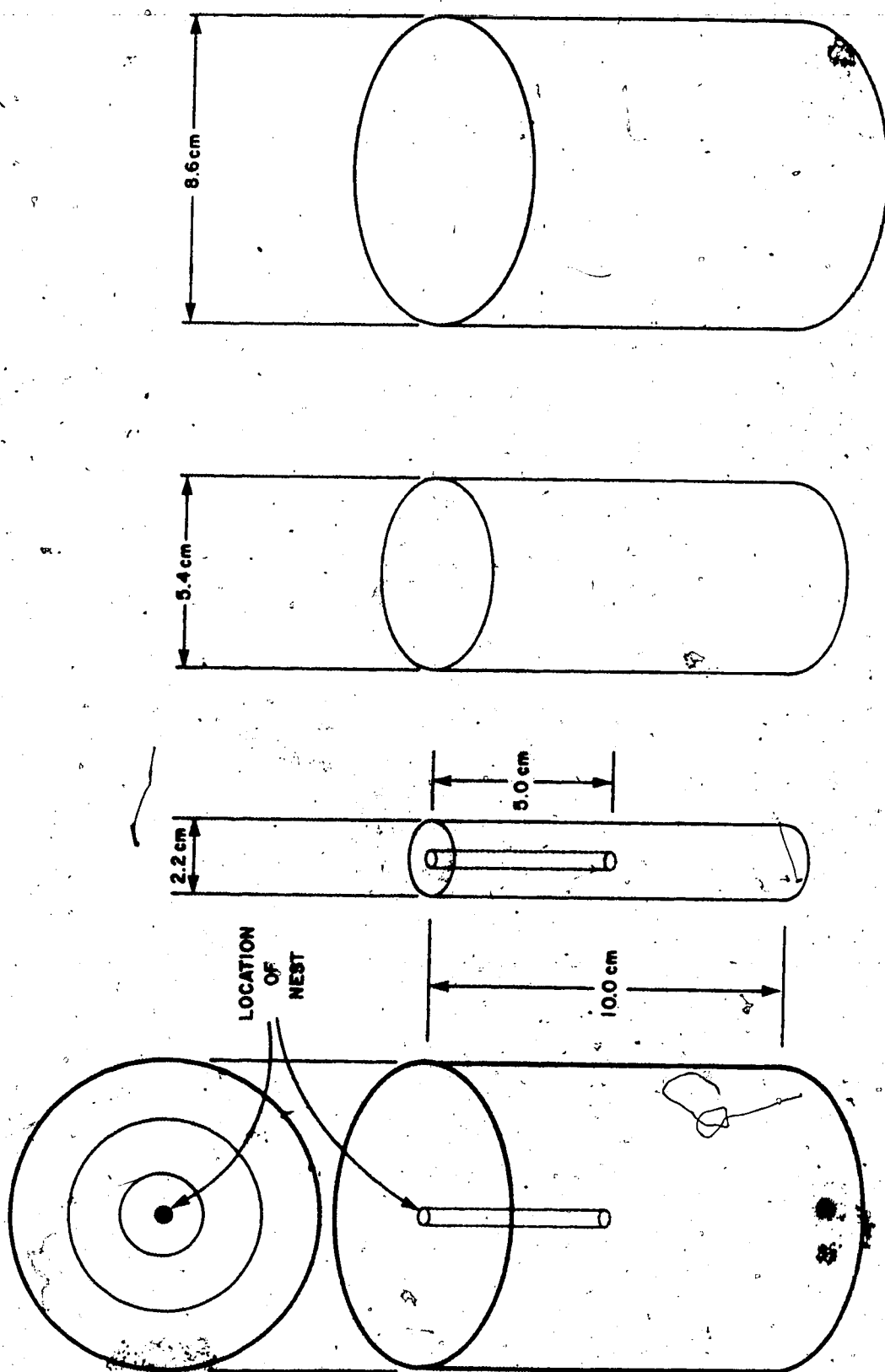


FIGURE 7. SOIL SAMPLES TAKEN WITH CONCENTRIC CYLINDERS IN A POT CONTAINING 500 g OF SOIL WHERE UREA WAS PLACED IN A NEST.

respectively. At about 4 cm from the nesting zone, 40 and 100 ug N/g soil accumulated as urea and ammonium respectively. Nitrate and nitrite contents increased slightly to 11 and 0.9 ug N/g soil respectively. After 15 days, urea was completely hydrolyzed and only inorganic forms of N were found. The ammonium concentration in the nesting zone was increased to 167 ug N/g soil; nitrate and nitrite contents were 7 and 1.8 ug N/g soil, respectively. At about 2 cm from the nesting zone, there was a peak of NH_4^+ of 490 ug N/g soil, while 40 and 8 ug N/g soil were present as NO_3^- and NO_2^- , respectively.

At the end of the 25-days incubation period, the nesting zone had 100 ug N/g soil as NH_4^+ and only 14 ug N/g soil as NO_3^- . Again, the peak in ammonium of 292 ug N/g soil was found to be at about 2 cm from the nesting zone, whereas, that of NO_3^- and NO_2^- was at 4 cm.

While the pots with urea mixed into the soil were not sampled as in the foregoing, one would suppose that the urea diffused homogeneously through the soil particles.

The same type of incubation was conducted using a Chernozemic soil sample in pots containing 500 g, 1000 g and 2000 g of soil. Transformation and diffusion of urea followed a similar pattern to the one already described for the Luvisolic soil.

In summary, urea and ammonium moved very rapidly from the nesting zone towards the adjacent cylindrical soil section. This zone accumulated, at all times the largest

concentration of urea and ammonium. Although these two N forms also moved to the farthest soil section in the pot, the amount that moved was not as great as was that from the nesting zone to the zone immediately adjacent. Nitrification of urea in the nesting zone was almost negligible; this process was restricted to the external soil sections of the pot. NO_2 accumulated with a maximum peak in the most external section of soil, (at 4 cm from the nesting zone), after 25 days of incubation.

4.4 Hydrolysis of fall applied urea

Table 8, shows that urea applied during the first week of October and mixed into the soil, was not completely hydrolyzed until after November at sites 2 and 3. At site 1, one kg urea-N/ha was still detected in January.

Urea applied in October and placed in nests, was not hydrolyzed completely until after January at sites 2 and 3. At site 1, one kg urea-N/ha was still detected in March.

Urea applied in November, and mixed into the soil, decreased the rate of hydrolysis. By March, sites 1 and 2, had 3.8 and 1 kg urea-N/ha, respectively. Urea was not detected in March at site 3.

4.4.1 Effect of urea concentration and soil temperature on urease activity

Table 8. Recovery of urea-N, (kg/ha), after its application to the plots in the fall of 1977. Urea was applied at a rate of 56 kg N/ha.

Treat- ment**	Site 1		Site 2		Site 3	
	Nov.19	March4	Nov.25	March 6	Nov.12	March 8
<i>Mix</i>						
7-10 Oct.	2.0b*	0.0b	1.8 a	0.0a	1.3c	0.0c
22-25 Oct.	4.1a	0.0b	2.7a	0.0a	2.4b	0.0c
3- 6 Nov.		3.2a		1.0a		0.0c
<i>Nest</i>						
7-10 Oct.	3.5a	1.0b	2.8a	0.0a	4.1a	0.0c

* Within columns, values not followed by the same letter are significantly different from each other ($p=0.05$).

** Treatment = Time and method of application.

Based upon the results described above, assays were conducted in the laboratory to examine the effect of soil temperature and increasing urea concentration on urease activity. Michaelis constant (K_m) values for urease were calculated for both the Gray Luvisolic and the Black Chernozemic soil samples. This was done to test the hypothesis that the accessibility of the enzyme to the substrate in the two soils varied.

Figure 8, shows the rate of hydrolysis for the Gray Luvisolic soil samples, at different urea concentrations and at different soil temperatures. Urease activity increased almost linearly with increasing urea concentration up to 5 mM. At all soil temperatures the enzyme activity was maximum at a concentration of 5 mM urea in solution. Substrate concentrations greater than 10 mM urea, resulted in a subsequent decrease in urease activity. There was complete inhibition of enzyme activity at a concentration of 80 mM urea. Soil temperature, also influenced urease activity. At a concentration of 5 mM urea, the activity of urease at -5 C, 0 C, 10 C and 20 C was only 5%, 27%, 36% and 68%, respectively of that at 30 C (Figure 8).

When Black Chernozemic soil samples were incubated at 0 C and at 30 C, there was greater activity of urease at the higher temperature (Figure 9). When the concentration of urea was increased to 80 mM urea, the complete inhibition of urease shown by the Luvisolic sample, was not present in the Black soil.

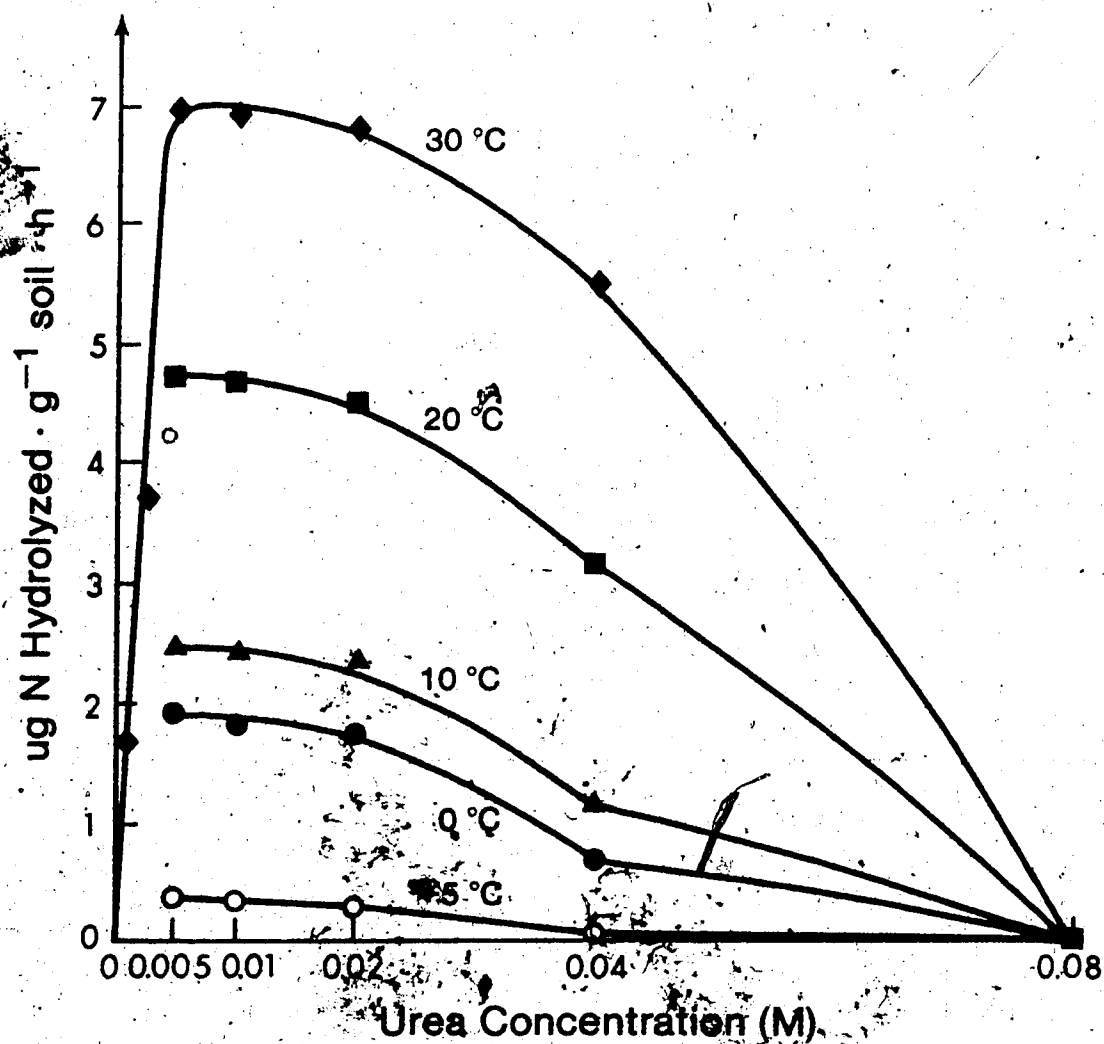


Figure 8. Effect of soil temperature and urea concentration on the urease activity of a Luvisolic soil.

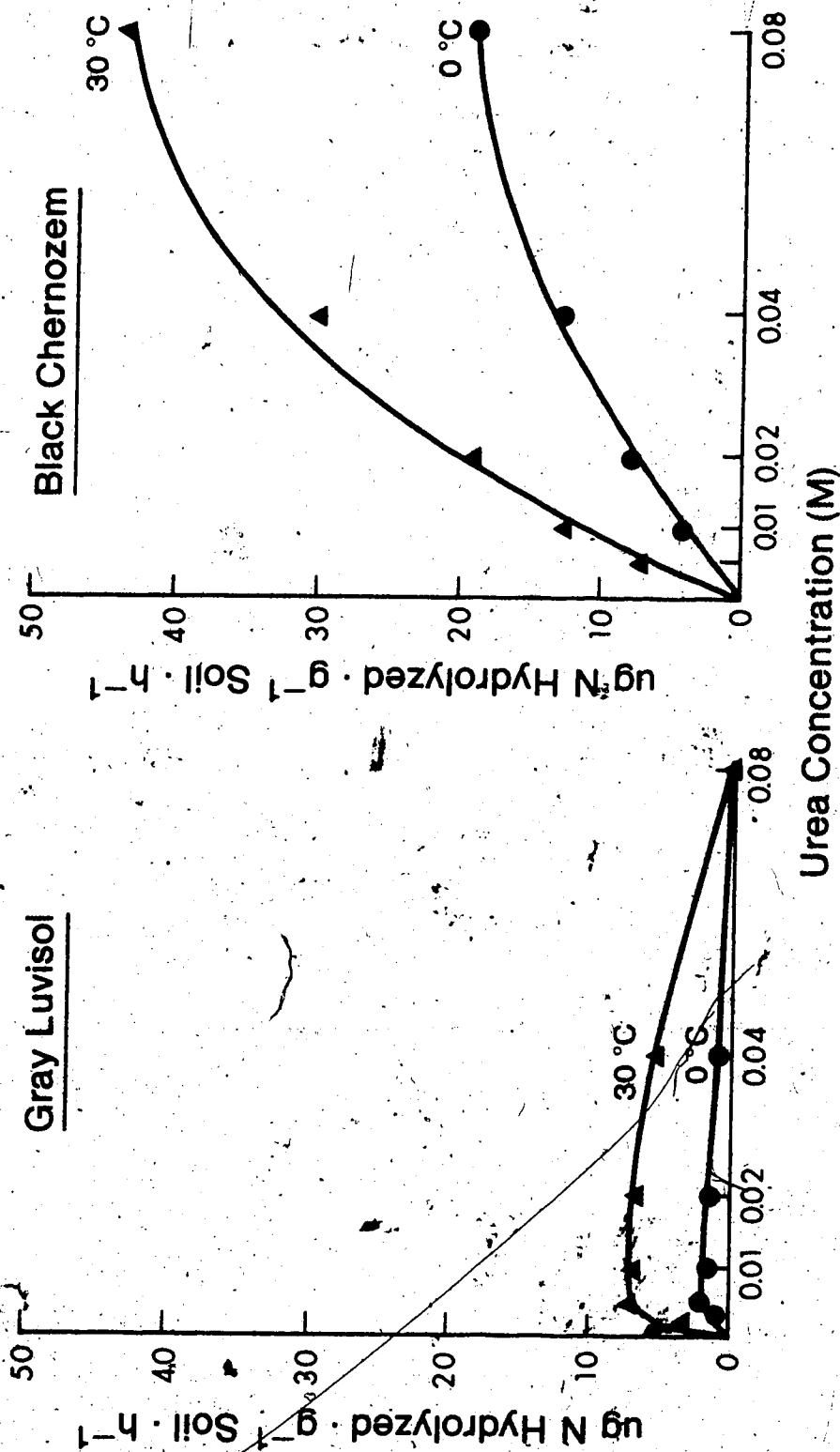


Figure 9. Effect of soil temperature and urea concentration on the activity of the urease in both, the Gray Luvisolic and the Black Chernozemic soil samples.

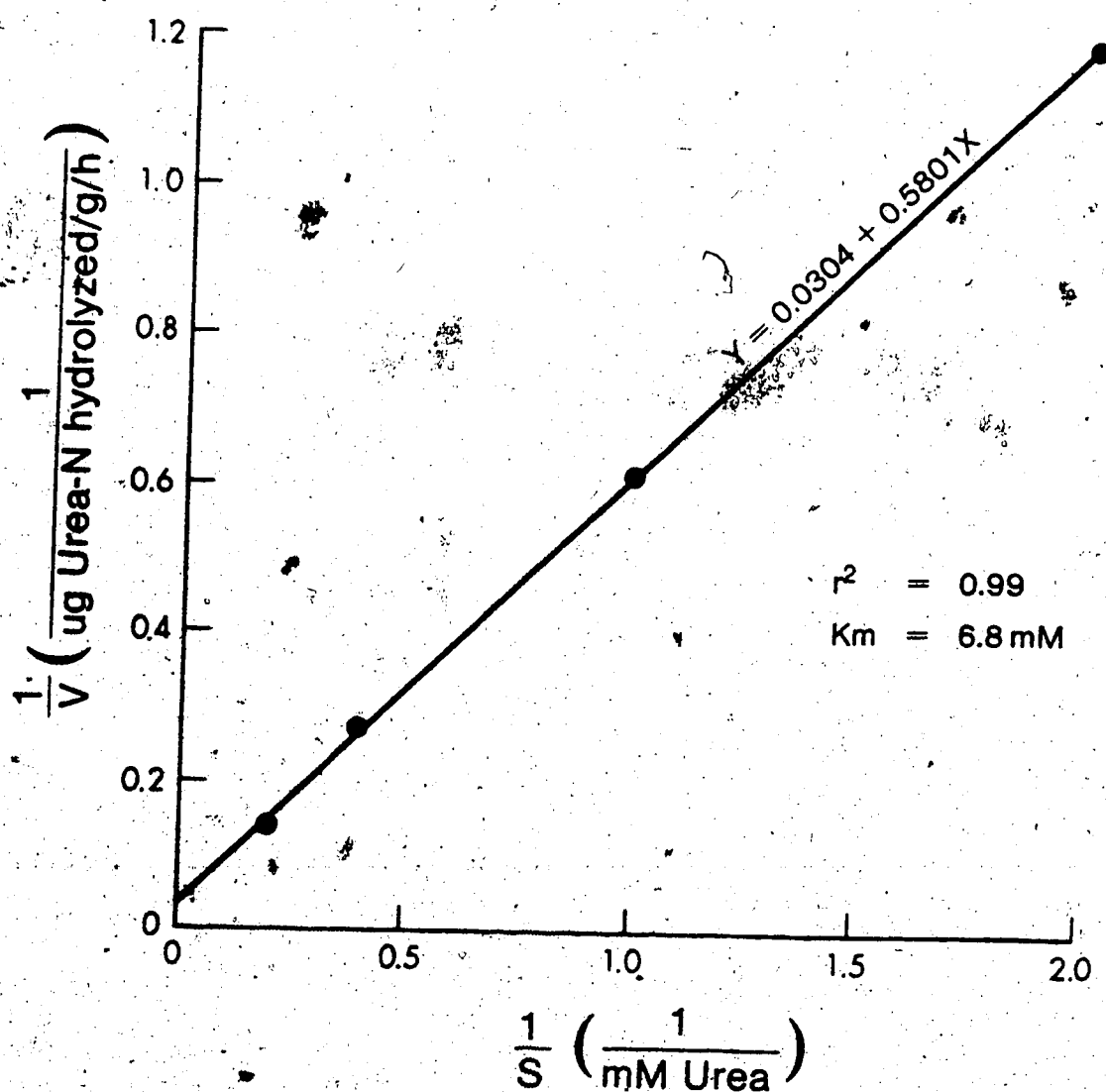


Figure 10. Lineweaver-Burke plot of urease activity at 30°C in the Gray Luvisolic soil.

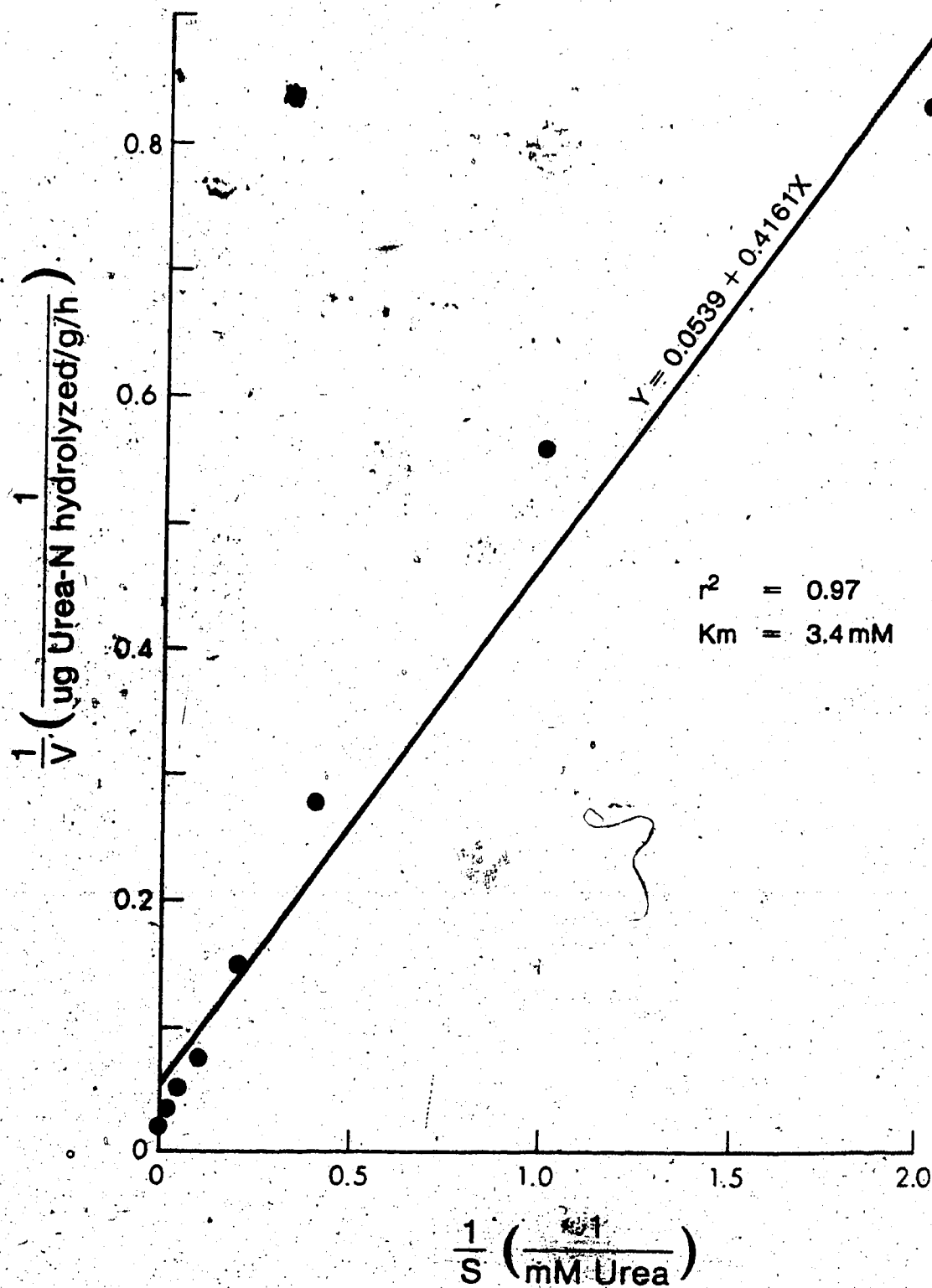


Figure 11. Lineweaver-Burke plot of urease activity at 30 °C in the Black Chernozemic soil.

K_m values obtained for the Luvisolic and the Chernozemic soils, were 6.8 mM and 3.4 mM, respectively, implying a greater accessibility of the enzyme to the substrate in the latter soil (Figures 10 and 11).

These results strongly suggest that soil temperature, substrate concentration and some unknown soil factor affect urease activity. Decreasing the soil temperature, resulted in less activity of urease. However, enzyme activity still existed at soil temperature as low as -5 °C. Increasing the urea concentration up to 80 mM, produced a complete inhibition of urease in the Luvisolic soil and only reduced its activity in the Chernozemic soil. K_m values confirmed a greater affinity of the enzyme for the substrate in the latter soil.

After elucidating some of the dynamics and reactions of fertilizer N placed in nests, it is worthwhile to evaluate and quantify the effects exerted by nest placement of fall applied N fertilizers on the yield and N uptake of a barley crop, established at three different sites.

4.5 Grain yield and N uptake as affected by various factors

4.5.1 Effect of methods of fertilizer placement and time of fertilization on yield increase.

At site 1, urea applied in early, mid and late fall, mixed into the soil, gave yield increases equivalent to 47%, 60% and 57%, respectively, of that obtained from spring

applied urea which was mixed into the soil (Table 9).

Urea applied in bands in mid fall, at spacings 30 cm and 60 cm, gave yield increases of 62% and 65% respectively of that obtained from spring applied urea, mixed into the soil (Table 9).

However, urea applied in early, mid and late fall, and placed in nests at 60 cm x 60 cm spacing, gave yield increases of 59%, 84% and 78%, respectively of that obtained from spring applied urea (Table 9).

At site 2, urea applied in early, mid and late fall, mixed into the soil, gave a yield increase of 40%, 59% and 70%, respectively of that obtained from the spring applied urea (Table 10).

Urea applied in bands in mid fall, at spacings of 30 cm and 60 cm, gave yield increases of 76% and 60%, respectively of that obtained from spring application. However, urea applied in early, mid and late fall, placed in nests at 60 cm x 60 cm spacing, gave yield increases of 71%, 75% and 70%, respectively of that obtained from the spring applied urea. Nests spaced at 30 cm x 30 cm gave a yield increase of 82% of that obtained from spring applied urea (Table 10).

At site 3, urea applied in early, mid and late fall, mixed into the soil gave yield increases of 51%, 62% and 72%, respectively of that obtained from the spring application (Table 11).

Urea applied in mid fall, placed in bands at spacings 30 cm and 60 cm gave yield increases of 79% and 70%,

Table 9. At site 1, the effect of type, method and time of application of fertilizer N on the yield increase and N uptake of barley crop. Fertilizers applied at a rate of 56 kg N/ha.

Time of application	Fert.	Method of application	Increase in yield 100 Kg/ha	Total net N uptake kg/ha
7 Oct.	Urea	Mix	*9.2 b	18.0 bcd
		Nest (60 cm apart)	11.7 b	24.8 abc
22 Oct.	Calcium nitrate	Mix	9.0 b	12.7 d
	Urea	Mix	11.9ab	20.4abcd
		Band (30 cm)	12.3ab	22.2 abc
		Band (60 cm)	12.8ab	21.2 abc
		Nest (30 cm apart)	11.9ab	30.2 ab
		Nest (60 cm apart)	16.5ab	30.5 a
	Ammonium sulfate	Mix	15.6ab	25.7 abc
		Nest (60 cm apart)	12.3ab	25.9 abc
3 Nov.	Urea	Mix	11.2 b	17.3 cd
		Nest (60 cm apart)	15.4ab	28.5 abc
31 May	Urea	Mix	19.7 a	32.5 a
		Control	8.1	18.2
Stand.	Error		2.3	3.8

** Yield increase = yield of treatment - yield of control
 Tot. net N uptake = N uptake of treatment - N uptake of control

* Within columns, values not followed by the same letter are significantly different from each other ($p=0.05$).

Table 10. At site 2, the effect of type, method and time of application of fertilizer-N on the yield and N uptake of barley crop. Fertilizers applied at a rate of 56 kg N/ha.

Time of application	Fert.	Method of application	Increase in yield 100kg/ha	Total net N uptake kg/ha
8 Oct.	Urea	Mix	*7.7 e	17.4 d
		Nest (60 cm apart)	13.7 c	28.7 c
23 Oct.	Calcium Nitrate	Mix	7.8de	12.7 d
	Urea	Mix	11.3cde	31.1 c
		Band (30 cm)	14.7 bc	34.8bc
		Band (60 cm)	11.6 cd	31.8/c
		Nest (30 cm apart)	15.9abc	38.2bc
		Nest (60 cm apart)	14.4 c	37.4bc
	Ammonium sulfate	Mix	11.9cde	29.5ab
		Nest (60 cm apart)	20.2 a	52.0 a
4 Nov.	Urea	Mix	13.5 c	32.0 c
		Nest (60 cm apart)	13.5 c	33.0 c
1 June	Urea	Mix	19.3ab	49.6 a
Stand.	Error	Control	14.7	35.8
			1.6	3.9

* Within columns, values not followed by the same letter are significantly different from each other ($p=0.05$).

respectively of that obtained from spring applied urea. Urea applied in early, mid and late fall, placed in nest at spacing 60 cm x 60 cm, produced yield increases of 135%, 90% and 94%, respectively of that obtained from the spring applied urea, mixed into the soil (Table 11).

The values in Tables 9, 10 and 11, show that nest placement of nitrogen fertilizers applied in the fall, gave higher yield increases as compared to mixing the fertilizers into the soil at the different times of application. Out of a total of 15 comparisons (nest versus mix) made at the three sites, 12 show higher yields when N fertilizers were nested. Three of these 12 comparisons were significantly different as shown by Duncan's test. In 2 out of the 15 cases, nested and mixed treatments of N fertilizers produced identical yield; and only in 1 case, the mixed N fertilizers gave a higher yield, although it was not significantly different.

The same tables show that of a total of 12 comparisons (nest versus band) at the 3 sites, there were 9 cases in which urea placed in nests gave the higher yields and 3 cases in which banding was superior. These differences were not significantly different.

4.5.2 Effect of different types of N fertilizers on yield increase

At site 1, when N was applied in mid fall as $\text{Ca}(\text{NO}_3)_2$ and mixed into the soil, it gave a yield increase of only

Table 11. At site 3, the effect of type, method and time of application of fertilizer-N on the yield increase and N uptake of barley crop. Fertilizers applied at a rate of 56 kg N/ha.

Time of application	Fert.	Method of application	Increase in yield 100 kg/ha	Total net N uptake kg/ha
10 Oct.	Urea	Mix Nest (60 cm apart)	*8.6 cd 22.9 a	18.7 fg 59.6 a
25 Oct.	Calcium nitrate	Mix	8.0 d	11.7 g
	Urea	Mix Band (30 cm) Band (60 cm) Nest (30 cm apart) Nest (60 cm apart)	10.5 bcd 13.4 bcd 11.9 bcd 15.2abcd 15.1abcd	23.6 efg 30.7 cdef 24.9 efg 36.4bcde 38.1bcde
	Ammonium sulfate	Mix Nest (60 cm apart)	14.8 bcd 16.6 ab	37.0 bcd 41.1 abc
6 Nov.	Urea	Mix Nest (60 cm apart)	14.8 bcd 15.9 abc	28.8 def 34.5bcdef
1 June	Urea	Mix	17.0 ab	46.0 ab
Stand.	Control		17.5	41.1
	Error		2.3	4.4

* Within columns, values not followed by the same letter are significantly different from each other ($p=0.05$).

46% of that obtained from spring applied urea, mixed into the soil.

Ammonium sulfate, applied in mid fall, mixed into the soil, produced a yield increase of 79% of that obtained from spring applied urea, mixed into the soil. Increases produced by application of urea, mixed into the soil have been already described.

At site 2, application of $\text{Ca}(\text{NO}_3)_2$ in mid fall, gave a yield increase of only 40% of that obtained from spring applied urea. The $(\text{NH}_4)_2\text{SO}_4$, mixed into the soil in mid fall, behaved like urea applied in mid fall and mixed into the soil.

At site 3, $\text{Ca}(\text{NO}_3)_2$ mixed into the soil, gave a yield increase equivalent to 47% of that obtained from spring applied urea, mixed into the soil. Ammonium sulfate, mixed into the soil produced similar effects on yield increases, as the produced by urea mixed into the soil.

Calcium nitrate produced lesser yield increases than did ammonium sulfate and urea when these fertilizers were applied in the fall and mixed into the soil. Usually, these differences were not significantly different. Ammonium sulfate and urea applied in the fall behaved somewhat similarly when they were nested.

4.5.3 Effect of nest placement on N uptake

The results of Tables 9, 10 and 11, show that almost for every location and for every time of fertilization, urea

applied in the fall and placed in nests induced greater N uptake than did urea applied in the fall placed in bands or mixed into the soil. However, these differences were often not statistically significant. Average values of N uptake at all three sites were taken for calculations on mid-fall urea treatments. Values for mixing the urea into the soil, for placement in bands, and for placement in nests were 59%, 55% and 82%, respectively, with uptake for spring application set as 100%. Statistical analyses was not performed on these uptake data, where all sites were taken together.

The yield information of the three sites was summarized and is shown in Table 12. Treatments were combined based on the method of placement and time of application. For example, an average was obtained from all the 36 observations of the nested urea treatments across all sites, while the average of all treatments across sites was made up of only 9 observations in the case of $\text{Ca}(\text{NO}_3)_2$. Statistical analyses are not presented, because this analyses may not be appropriate for these results. Consequently, the results in Table 12, are only given with that caution kept in mind.

There are broad differences in yield increases from the lowest yield to the highest-yielding treatment, with the yield increase of 830 kg/ha of barley grain from the fall applied $\text{Ca}(\text{NO}_3)_2$ treatment to 1870 kg/ha on the spring-applied urea treatment (Table 12). Another way of viewing the results is to assign the yield increase of the highest-yielding treatment, (i.e. spring applied urea), a

value of 100%, and evaluating the yield increases of the other treatments as percentages of the spring applied urea. Thus, the fall-applied $\text{Ca}(\text{NO}_3)_2$ gives only a yield increase of 44%. For the fall-applied urea when mixed into the soil, when banded, or when nested the values are 58, 67, and 81% respectively. This points out that the yield from fall-applied urea is improved when the fertilizer is nested rather than mixed.

Table 12. Average of the three field trials, showing the effect of type, method and time of application of fertilizer-N on the yield increase of the barley crop. Fertilizers added at a rate of 56 kg N/ha.

Time of application	Fertilizer	Method of application	Average yield increase of all sites (100 Kg/ha)
Fall	Calcium nitrate	Mix	8.3 (9)
Fall	Urea	Mix	11.0 (27)
Fall	Urea	Band	12.8 (18)
Fall	Urea	Nest	15.2 (36)
Fall	Ammonium sulfate	Mix	14.1 (9)
Fall	Ammonium sulfate	Nest	16.4 (9)
Spring	Urea	Mix	18.7 (9)
	Control		13.6 (9)

* () = number of observations used to calculate average value.

5. DISCUSSION

Mineralization of native organic N took place during the winter, from October to March in three different frozen soils of Alberta, and the rates of mineralization differed among the soils. There is a scarcity of information in the literature to support this finding. In spite of this, Alexander, (1965), suggested that there is little reason to doubt that there may exist a slow nitrification at temperatures lower than 2 C. Malhi (1978), found an accumulation of inorganic-N during winter in frozen soils of Alberta. Recent studies reported by Malhi and Nyborg (1979b), showed an accumulation of nitrates from fall applied urea in frozen soils of Alberta. A microbial study conducted by Mekhtiev (1972), in a northern region of the USSR, showed a larger population of nitrifying organisms during winter than during summer or fall.

Soil temperature and moisture determinations for each site, during the winter months, indicate that the first 15 cm of soil were frozen and that the moisture content (O.D.B.) of the soils ranged between 25% and 38% (Table 13 and 14). Also soil temperatures, registered daily during the winter at the Ellerslie meteorological station, showed the first 15 cm of soil were at temperatures slightly below the freezing point (-1 to -6), and that soil temperatures increased or decreased from one day to another. This fluctuation in temperature, may exert on the soil organic matter an effect similar to that described by Ivarson and

Table 13. Soil temperature (C) at three different soil depths at the three sites of experimentation during 1977-1978.

Location	Date	Soil temperature at different depths		
		7.5 cm	15 cm	30 cm
Breton	Nov. 6, 1977	0.5	1.0	2.0
	Nov. 19, 1977	-0.5	0.0	1.0
	Jan. 28, 1978	-1.5	-1.2	-1.0
	Feb. 9, 1978	-2.8	-2.2	-1.7
	Feb. 26, 1978	-2.5	-2.0	-1.5
	March 4, 1978	-5.0	-4.5	-3.2
	March 27, 1978	0.0	0.0	0.0
	April 1, 1978	0.1	0.5	0.0
	April 8, 1978	4.7	1.9	0.5
	April 25, 1978	12.0	8.0	4.5
Westlock	Nov. 12, 1977	0.5	0.5	1.5
	Nov. 25, 1977	-1.0	0.5	1.0
	Dec. 30, 1977	-2.5	-2.3	-1.5
	Feb. 11, 1978	-3.5	-3.0	-2.0
	Feb. 26, 1978	-4.0	-3.5	-2.5
	March 10, 1978	-1.0	-1.0	-1.7
	March 27, 1978	1.0	0.0	0.0
	April 1, 1978	0.0	0.0	0.1
	May 19, 1978	20.0	15.0	10.0

continue.

Bo. Accord	Nov. 12, 1977	0.0	0.0	1.0
	Nov. 25, 1977	-1.5	-1.0	0.7
	Dec. 30, 1977	-4.0	-3.0	-2.0
	Jan. 28, 1978	-3.5	-2.0	-2.5
	Feb. 9, 1978	-2.2	-2.2	-1.8
	Feb. 26, 1978	-2.0	-1.7	-1.0
	March 9, 1978	-1.2	-1.9	-2.1
	March 27, 1978	0.5	0.0	0.0
	April 1, 1978	5.0	5.0	5.0
	April 27, 1978	10.5	8.0	5.0
	May 20, 1978	13.0	11.0	8.5

Table 14. Soil moisture (O.D.B.) at four different depths during 1977-78.

		Soil moisture (%) at different depths			
Location	Date	0-15cm	15-30cm	30-60cm	60-90cm
Breton	Oct. 1, 1977	15.7	20.0	13.4	15.9
	Nov. 1, 1977	23.2	22.4		
	Dec. 31, 1977	26.4	19.7		
	Feb. 25, 1978	28.4	20.2		
	March 8, 1978	25.8			
	April 25, 1978	22.0	19.4	22.1	24.0
	May 12, 1978	20.4	19.8	15.8	25.4
Westlock	Oct. 1, 1977	18.3	23.0	20.2	21.7
	Nov. 1, 1977	24.0	18.5		
	Dec. 30, 1977	25.0			
	Feb. 25, 1978	36.0	23.0		
	March 9, 1978	29.6	24.5		
	April 19, 1978	28.2	30.0	32.9	32.5
	May 14, 1978	29.0	22.0	28.1	26.3
Bon Accord	Oct. 1, 1977	30.0	28.0	34.3	32.7
	Nov. 1, 1977	31.0	28.7		
	Dec. 30, 1977	26.0	25.0		
	Feb. 25, 1978	38.1	26.4		
	March 10, 1978	43.0	28.0		
	May 16, 1978	33.7	30.2	27.4	35.4

* There was free water on soil surface and frozen ground below 35 cm between the 1st and the 8th of April at Breton, Westlock and Bon Accord. Free water on soil surface remained until the end of April at the latter place.

Sowden (1970). They found that freezing of soil samples at -14 C for three weeks, caused a marked increase in the total amount of free amino acids and sugars, and that after the third week, the content of these organics disappeared dramatically. Freezing also increased the amount of mineralized N (Mack, 1963). Soulides and Allison, (1961), indicated that the increase in decomposition of the soil organic matter, followed by intermittent drying or freezing, is due primarily to the release of nutrients, especially energy sources that can be rapidly oxidized by the soil microflora.

Unfrozen films of water exist in frozen soils (Murrman et al., 1968); and this unfrozen water surrounds the soil mineral grains in a zone that ranges in thickness from 3 to 50 A or more. This has been shown to occur at temperatures as low as -10 C to -50 C (Anderson and Tice, 1971). Substrates such as amino acids and other nitrogenous compounds that are released from the organic pool by soil freezing could thus remain concentrated and dissolved in the unfrozen films of water. Those microbial cells which remain active at the lower temperatures would be able to oxidize a greater percentage of this organic substrate to completion than those active at higher temperatures (Ivarson and Sowden, 1970).

Based on this information, it is suggested that two main processes or a combination of them might be involved in the mineralization of organic matter in frozen soils. The

first is represented by microbial metabolism, which can accumulate mineral-N as a waste product in the soil environment. The second, represented by freeze-thaw cycles occurring in the top of the soil during winter. This physical phenomena could depolymerize complex organic substrates into lower molecular weight and more assimilable organic compounds, which will favour the microbial activity. Freezing and thawing also destroys a portion of the soil microbial biomass. The dead cells are susceptible to further lytic action by enzymes or predators, processes that can facilitate N mineralization in frozen soils. Larger microorganisms, such as protozoa, would be more susceptible to destruction, making the soil environment less competitive and more favourable for the growth and activity of heterotrophs. Further studies are needed to examine this theory.

Urea is frequently used for fall application of N fertilizers in Alberta. Urea hydrolyses very rapidly after its application to soils, usually within a few days after applied (Tisdale and Nelson, 1975). However, in the present study, the hydrolysis of urea applied in fall was affected by soil temperature (time of application) and the method of application (nested, banded or mixed into the soil) (Table 8).

The amount of urea recovered in March, four months after its application to the soil, indicates that the rate of hydrolysis was indeed affected by lower soil

temperatures. When urea was mixed into the soil in early October, the soil temperature at the three sites ranged between 6 and 8 C and the urea was hydrolyzed very rapidly. However, when urea was mixed into the soil in November with the soil temperature at about 0 C, urea was still detected in March at site 2. Since the hydrolysis of urea is mainly an enzymatic reaction (Bremner and Mulvaney, 1978), there is little doubt that temperatures of 0 C and below affected the activity of the enzyme. The incubation experiments carried out in the laboratory, also demonstrated a decrease in urease activity with decreasing soil temperature.

Increasing concentration of substrate (urea) resulted in an inhibition and a reduction in the activity of urease in the soil. Results obtained from the incubation of a Luvisolic soil sample with increasing urea concentration showed that the enzyme was inhibited by substrate concentrations of 5.0 mM urea and higher. Inhibition of the enzyme by substrate has been reported only with pure homogeneous systems (Laidler and Hoare, 1949). The inhibitory effect is attributed to the existence of two neighboring sites in the active center of the urease molecule one of which binds urea and the other water. At high urea concentration, the substrate is adsorbed on the water site (Bull, 1971).

With the same substrate concentrations, the Chernozemic soil sample showed only a decrease in enzymatic activity at 80 mM urea. The difference in enzymatic activity between

these two soils might be due to a lower concentration of urease in the Luvisolic soil or to undetermined factors (adsorption and/or diffusion) affecting the affinity of the enzyme and substrate in the latter soil. This was reflected in the K_m values of 3.4 mM for the Chernozemic soil as compared to 6.8 mM obtained for the Luvisolic soil. Field experiments showed that urea was also hydrolyzed at a higher rate at the sites with Chernozemic soils. The effect of substrate concentration on urease activity is particularly important from an agronomic point of view. It may help to explain, in part, the positive effect of urea placed in nests on the efficiency of fall applied nitrogen fertilizers. Indeed, the highly concentrated form of N enhanced the conservation of the fertilizer N in the soil during the critical time of spring thawing by slowing down the hydrolysis rate and subsequently reducing the nitrification process during winter and early spring.

Since N fertilizers applied in fall are less efficient than when applied in spring, due to significant denitrification losses occurring in early spring (Nyborg et al., 1977), it is of primary importance to avoid the accumulation of nitrate in the soil during winter, so that only a minimum of substrate, or none, is available for the denitrifying organisms during the spring thaw.

Urea mixed into the soil may undergo a very rapid nitrification process (Tisdale and Nelson, 1975; Alexander, 1977). However, less of the nested urea applied in fall was

nitrified by March, than of the urea mixed into the soil (Table 3). This effect was shown consistently at the three sites of experimentation. Incubations made in the laboratory, confirmed that urea placed in nests was nitrified at a much slower rate than was urea mixed into the soil (Table 4). Urea placed in nests, greatly affected the growth and activity of *Nitrosomonas* and *Nitrobacter* in the soil. The mechanism by which this occurred was not determined, but factors such as electrical conductivity of the soil and soil pH were not associated with the variations in population sizes of these autotrophs. This was conclusively shown by the results obtained from the incubation experiments.

The growth or activity of *Nitrobacter* could have been affected by: a) Ammonium toxicity; b) Nitrite toxicity; or c) [redacted] effects caused by some soil organic compounds. [redacted] are inhibited at high ammonium concentration due to a selective toxic effect of the substrate on these autotrophs (Alexander, 1977). Nitrite concentration of 130 ppm and more may also have a deleterious effect on the growth of *Nitrobacter agilis* (Aleem and Alexander, 1960). However, determination of the nitrifying population in soil samples with urea placed in nests, showed that cells of *Nitrobacter* were killed and their growth was inhibited in areas far from the nesting zone, where NH_4 and NO_2 diffused at extremely low concentrations. In the area involving the nesting zone,

where ammonium content was extremely high, the growth of *Nitrobacter* was enhanced (Figure 4). Since ammonium and nitrite were in low concentrations in areas far from the nesting zone and the N recovery was almost complete, the possibility of NH_4 toxicity was not considered feasible. Therefore, factors (a) and (b), do not appear to directly cause the decrease in nitrification rate of the urea placed in nests. The third possibility appears to be more reasonable. Urea placed in nests has been shown to accumulate as ammonium in large concentrations, which in the presence of water, combines to form ammonium hydroxide. The latter, an organic solvent, might have dissolved and diffused through the soil some low molecular weight aromatics and or phenolic compounds, such as catechol, quinhydrone, hydroxylamine and others. These organic compounds have been proven to be inhibitors of nitrification and some of them can have a residual effect on *Nitrobacter* cells (Lees and Quastel, 1946). In the area close to the nesting zone, these organics would precipitate due to the high salt concentration (E.C. = 13.5 mmhos/cm), thus causing no deleterious effect on the *Nitrobacter* cells. Nevertheless, if some of these compounds diffused to areas far from the nesting zone, they will not precipitate due to a lower salt concentration (E.C. = 2 mmhos/cm), but would kill and inhibit the growth of *Nitrobacter* cells. This hypothesis coincides with the experimental results obtained from the field trials during the study.

On the other hand, urea mixed into the soil brought an enrichment of the *Nitrobacter* population during all the incubation periods (Table 6). As a result a more active population developed, which enabled a higher rate of oxidation of ammonium salts to nitrate.

The recovery of N from urea applied in nests was always greater than the recovery of N from urea mixed into the soil. When urea is mixed into the soil, it diffuses very rapidly through the porous media. As a result, an intimate contact between soil particles and urea is obtained, thus, facilitating biological activity on this substrate. When mineral-N is inadequate to fulfil the metabolic requirements of growing organisms decomposing organic matter, these heterotrophs assimilate inorganic N to build their cell structures, so that the plant availability of N provided through fertilizers, can be reduced temporarily through immobilization. However, since urea placed in nests is a very concentrated and localized fertilization, the contact between urea and soil particles is reduced greatly, thus reducing biological activity on the substrate. During winter, under field conditions when most of the soil water is frozen, the diffusion of urea from the nesting zone is greatly affected, so that under conditions of N deficiency, fertilizer N is subject to little or no immobilization. Incubation studies carried out in the laboratory confirmed these observations. Also the difference in N recovery among the two methods of application can be attributed to a

reduction of the gaseous N losses by nest placement in conditions of soil water saturation.

Avoiding N losses by denitrification and immobilization processes, among others, will inevitably allow more efficient use by plants of fall applied N fertilizers. In the present study, this was reflected by yield increments, (some significant and some not), produced by barley in plots where fall applied N fertilizers were placed in nests (Table 12). Variation due to sites was not significant and accounted for only 15% of the the total variation in yield; therefore the variations in yield were a result of the different treatments. In almost all cases, nitrogenous fertilizers applied in fall and placed in nests produced higher, (although not significant) N uptake, compared to the uptake obtained when N fertilizers were mixed into the soil in the fall.

This study produced two other observations which deserve mention. The first is that at Bon Accord, urea applied in fall and placed in nests gave a significantly higher yield increase (at $p=0.05$), than did urea applied in the spring and mixed into the soil. This was consistently shown by all replicates. The second is that at Breton, yields did not show consistent and significant differences between nest and mix treatments. Factors like rate of N fertilizer, other nutritional deficiencies or other environmental factors could have masked the effect of nest placement.

The time of fertilization was shown to be important only when N fertilizers were mixed into the soil. Delaying fertilizer application in fall decreased the nitrification rate of the fertilizer so that denitrification losses could have been diminished.

Studies made on N uptake and yield increments when fertilizers are placed with different techniques, indicate that N availability for plants is enhanced when fertilizers are placed in bands (Sobulo et al., 1978; Tisdale and Nelson, 1975). However, in the present investigation, bands and nests were completely disrupted by soil cultivation soon before seeding. Hence, the positive effect of nest placement, on yield and N uptake, was not caused by the position of the fertilizer while the crop grew. Instead, the benefit for the crop occurred through the reducing losses of mineral N by keeping the N fertilizers away from immobilization during winter and/or from denitrification losses during the spring thaw.

Denitrification losses occur mainly from nitrate based fertilizers (Malhi, 1978). This effect was also evident in the present study, where plots fertilized with $\text{Ca}(\text{NO}_3)_2$ in fall, gave the lowest yield increase and lowest N uptake by barley. N recovery from soil samples of different treatments taken in March and April, strongly support this conclusion. $(\text{NH}_4)_2\text{SO}_4$ was superior to urea when applied in mid fall and mixed into the soil.

All the previous analyses of nest placement versus other application techniques, indicate that nest placement has obvious advantages for western Canadian agriculture. This new placement technique is a practical tool to enhance the efficiency of fall applied N fertilizers and can be used as an alternative to chemical inhibitors of nitrification.

6. CONCLUSIONS

The results obtained from the field trials and incubation studies, permit the following conclusions:

- a. Nest placement of N-fertilizers applied in fall increases the yield by reducing the mineral N losses. Out of 15 comparisons, of nest and mix treatments, in 12 cases nest placement of N fertilizers gave higher yields (only in 3 cases were these differences significant).
- b. Mineral N losses are minimized by nest placement due to a decrease in the rate of urea hydrolysis, and to a reduction in nitrate accumulation over the winter. The *Nitrobacter* population is especially affected by nest placement of urea.
- c. Time of N fertilization in autumn had no significant effect compared to placing the N fertilizers in nests.
- d. Calcium nitrate applied in fall produced lower yield increases and N uptake by barley than NH_4 based fertilizers. Ammonium sulfate and urea behaved similarly when they were applied in fall and mixed in nests.

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APPENDIX

'List of Appendix Tables'

Table 1. At site 1, the content of urea-N, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (kg/ha) in November in the top 15 cm of soil at different times in 1977-78. Urea applied at a rate of 56 kg N/ha.

Time of appli- cation	Treatment	Depth (cm)	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	Urea-N
7-10 Oct.	Control	0-15	11.4	7.4	0.0
	Mix	0-15	44.8	10.9	2.0
	Nest	0-15	59.9	10.2	3.5
22-25 Oct.	Mix	0-15	43.5	11.1	8.1
	Band	0-15	41.6	11.9	10.0

Table 2. At site 1, the content in January of urea-N, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (kg/ha), in the first 30 cm of soil in four treatments. Urea applied at a rate of 56 kg N/ha.

Time of appli- cation	Treatment	Depth (cm)	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	Urea-N
7-10 Oct.	Control	0-15	12.9	9.2	0.0
		15-30	4.4	1.1	0.0
	Mix	0-15	39.6	14.9	1.1
		15-30	9.8	4.6	0.0
22-25 Oct.	Band	0-15	44.4	13.6	5.4
3-6 Nov.	Mix	0-15	38.4	8.2	14.0
		15-30	12.0	4.6	0.0

Table 3. At site 1, the content of urea-N, NH₄-N and NO₃-N (kg/ha) in March, in the top 120 cm of soil. Urea applied at a rate of 56 kg N/ha.

Time of appli- cation	Treatment	Depth (cm)	NH ₄ -N	NO ₃ -N	Urea-N
7-10 Oct.	Control	0-15	16.3	10.5	0.0
		15-30	7.3	3.5	0.0
		30-60	6.1	3.3	0.0
		60-90	3.0	3.5	0.0
		90-120	0.9	0.0	0.0
	Mix	0-15	38.8	18.9	0.0
		15-30	13.5	8.9	0.0
		30-60	2.7	3.6	0.0
		60-90	2.7	5.4	0.0
		90-120	0.0	0.0	
	Nest	0-15	52.9	5.4	1.0
		15-30	18.2	9.7	0.0
		30-60	4.8	5.1	
		60-90	2.1	3.8	

		90-120	1.9	0.0	
22-25	Mix	0-15	49.6	16.8	0.0
Oct.		15-30	6.6	8.0	0.0
		30-60	4.7	5.4	
		60-90	2.7	4.5	
		90-120	4.5	0.6	
3-6 Nov.	Mix	0-15	54.0	13.7	3.8
		15-30	9.1	5.1	0.0
		30-60	2.7	3.6	
		60-90	4.5	3.5	
		90-120	0.0	3.6	

Table 4. At site 1, the content of urea-N, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (kg/ha) in April, in the top 120 cm of soil. Urea applied at a rate of 56 kg/ha.

Time of appli- cation	Treatment	Depth (cm)	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	Urea-N
7-10 Oct.	Control	0-15	4.0	10.5	0.0
		15-30	3.2	6.6	0.0
		30-60	3.6	2.4	
		60-90	1.8	0.3	
		90-120	1.8	0.0	
	Mix	0-15	15.5	33.9	0.0
		15-30	6.7	3.1	
		30-60	3.0	0.9	
		60-90	2.0	1.0	
		90-120	1.4	0.0	
	Nest	0-15	19.4	4.0	0.0
		15-30	26.3	14.2	
		30-60	3.3	4.7	
		60-90	2.0	2.1	

		90-120	1.6	0.0	
22-25	Mix	0-15	37.6	26.0	0.0
Oct.		15-30	1.6	2.2	0.0
		30-60	2.6	1.8	
		60-90	2.3	0.0	
		90-120	1.7	0.0	
	Band	0-15	28.1	11.5	0.0
		15-30	8.9	9.3	0.0
		30-60	11.7	2.7	
		60-90	4.5	0.0	
		90-120	1.8	0.0	
3-6 Nov.	Mix	0-15	34.5	21.9	0.0
		15-30	8.4	5.2	0.0
		30-60	2.9	4.5	
		60-90	1.9	1.6	
		90-120	0.7	0.0	

Table 5. At site 2, the content of urea-N, NH₄-N and NO₃-N (kg/ha), in November, in the top 15 cm of soil. Urea applied at a rate of 56 kg N/ha.

Time of appli- cation	Treatment	Depth (cm)	NH ₄ -N	NO ₃ -N	Urea-N
7-10 Oct.	Control	0-15	16.2	12.5	0.0
	Mix	0-15	34.9	36.4	0.0
	Nest	0-15	59.2	18.9	2.8
22-25 Oct.	Mix	0-15	43.3	28.2	2.7
	Band	0-15	49.3	25.5	3.0

Table 6. At site 2, the content of urea-N, NH₄-N and NO₃-N (kg/ha), in January, in the top 30 cm of soil. Urea applied at a rate of 56 kg N/ha.

Time of appli- cation	Treatment	Depth (cm)	NH ₄ -N	NO ₃ -N	Urea-N
7-10 Oct.	Control	0-15	11.7	17.7	0.0
		15-30	3.4	6.7	0.0
	Mix	0-15	28.1	38.7	0.0
		15-30	6.1	8.4	0.0
	Nest	0-15	58.5	16.6	0.8
		15-30	5.6	6.3	0.0
3-6 Nov.	Mix	0-15	38.7	18.1	11.4
		15-30	8.8	8.3	0.0

Table 7. At site 2, the content of urea-N, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (kg/ha), in March, in the top 120 cm of soil. Urea applied at a rate of 56 kg/ha.

Time of appli- cation	Treatment	Depth (cm)	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	Urea-N
7-10 Oct.	Control	0-15	15.2	23.2	0.0
		15-30	11.7	10.7	0.0
		30-60	3.1	8.1	
		60-90	3.9	13.8	
		90-120	4.7	3.2	
Mix		0-15	24.8	52.9	0.0
		15-30	7.5	20.7	0.0
		30-60	10.9	0.7	
		60-90	4.0	3.8	
		90-120	5.2	0.8	
Nest		0-15	65.9	22.9	0.0
		15-30	9.7	11.5	0.0
		30-60	2.6	4.7	
		60-90	2.0	3.7	

		90-120	9.3	6.2	
22-25	Mix	0-15	42.7	43.8	0.0
Oct.		15-30	6.8	19.8	0.0
		30-60	6.2	2.3	
		60-90	4.7	0.0	
		90-120	6.8	0.0	
	Band	0-15	51.0	38.4	0.0
		15-30	7.8	15.3	0.0
		30-60	3.0	5.4	
		60-90	6.2	3.5	
		90-120	5.1	0.0	
3-6 Nov.	Mix	0-15	49.2	35.8	1.0
		15-30	12.6	9.1	0.0
		30-60	2.3	3.1	
		60-90	8.1	5.5	
		90-120	6.0	0.9	

Table 8. At site 2, the content of urea-N, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (kg/ha) in April, in the top 120 cm of soil. Urea applied at a rate of 56 kg N/ha.

Time of appli- cation	Treatment	Depth (cm)	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	Urea-N
7-10 Oct.	Control	0-15	10.4	12.7	0.0
		15-30	3.2	5.1	
		30-60	2.1	0.8	
		60-90	2.5	0.2	
		90-120	2.3	0.0	
	Mix	0-15	8.8	36.1	0.0
		15-30	5.9	7.9	0.0
		30-60	3.1	1.3	
		60-90	4.1	0.3	
		90-120	3.0	0.0	
	Nest	0-15	24.6	38.3	0.0
		15-30	6.3	4.3	0.0
		30-60	3.4	2.3	
		60-90	4.5	0.4	

		90-120	3.5	0.0	
22-25	Mix	0-15	15.0	52.8	0.0
Oct.		15-30	3.1	5.5	0.0
		30-60	1.2	0.4	
		60-90	2.6	0.0	
		90-120	1.3	0.0	
	Band	0-15	29.1	27.8	
		15-30	3.5	7.0	0.0
		30-60	3.1	2.6	
		60-90	1.0	0.8	
		90-120	0.0	0.0	
3-6 Nov.	Mix	0-15	20.8	50.4	0.0
		15-30	3.1	6.8	0.0
		30-60	2.0	0.8	
		60-90	1.1	0.0	
		90-120	3.6	0.0	

Table 9. At site 3, the content of urea-N, NH₄-N and NO₃-N (kg/ha), in November, in the top 15 cm of soil.

Urea applied at a rate of 56 kg N/ha.

Time of appli- cation	Treatment	Depth (cm)	NH ₄ -N	NO ₃ -N	Urea-N
7-10 Oct.	Control	0-15	8.9	26.0	0.0
	Mix	0-15	25.1	50.7	1.3
	Nest	0-15	63.3	22.6	4.1
22-25 Oct.	Mix	0-15	38.4	38.6	0.0
	Band	0-15	41.2	32.3	6.8

Table 10. At site 3, the content of urea-N, NH₄-N and NO₃-N (kg/ha), in January, in the top 30 cm of soil.

Urea applied at a rate of 56 kg N/ha.

Time of appli- cation	Treatment	Depth (cm)	NH ₄ -N	NO ₃ -N	Urea-N
7-10 Oct.	Control	0-15	12.4	31.9	0.0
		15-30	12.4	18.2	0.0
	Mix	0-15	24.4	63.6	0.0
		15-30	16.5	11.6	0.0
	Nest	0-15	70.3	32.2	0.0
		15-30	1.9	13.2	0.0
22-25 Oct.	Band	0-15	51.1	49.0	1.0
		15-30	4.4	8.1	0.0
3-6 Nov.	Mix	0-15	42.1	41.5	6.9
		15-30	15.7	18.1	0.0

Table 11. At site 3, the content of urea-N, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (kg/ha), in March, in the top 120 cm of soil. Urea applied at a rate of 56 kg N/ha.

Time of appli- cation	Treatment	Depth (cm)	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	Urea-N
7-10 Oct.	Control	0-15	20.1	35.4	0.0
		15-30	16.2	12.9	0.0
		30-60	10.7	6.9	
		60-90	6.7	5.4	
		90-120	4.8	5.7	
	Mix	0-15	30.2	72.6	0.0
		15-30	12.6	18.0	0.0
		30-60	6.6	5.4	
		60-90	5.4	6.2	
		90-120	1.9	6.7	
	Nest	0-15	68.8	41.0	0.2
		15-30	11.5	10.8	0.0
		30-60	12.2	7.8	
		60-90	6.7	4.5	

		90-120	3.8	1.9	
22-25	Mix	0-15	36.9	66.3	0.0
Oct.		15-30	12.2	14.7	0.0
		30-60	18.1	4.7	
		60-90	5.4	6.7	
		90-120	3.8	1.0	
3-6 Nov.	Mix	0-15	48.4	58.8	0.8
		15-30	13.1	18.4	0.0
		30-60	12.4	6.9	
		60-90	7.8	4.5	
		90-120	2.9	0.0	

Table 12. At site 3, the content of urea-N, $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ (kg/ha), in May, in the top 120 cm of soil. Urea applied at a rate of 56 kg N/ha.

Time of appli- cation	Treatment	Depth (cm)	$\text{NH}_4\text{-N}$	$\text{NO}_3\text{-N}$	Urea-N
7-10 Oct.	Control	0-15	14.8	20.0	0.0
		15-30	11.0	9.8	0.0
		30-60	7.4	4.2	
		60-90	6.7	1.8	
		90-120	8.1	1.9	
	Mix	0-15	11.0	30.9	0.0
		15-30	9.2	19.8	0.0
		30-60	4.4	16.6	
		60-90	7.1	3.6	
		90-120	5.7	8.6	
	Nest	0-15	19.6	52.7	0.0
		15-30	12.2	10.7	0.0
		30-60	8.7	7.9	
		60-90	6.7	9.8	

		90-120	5.3	5.1	
22-25	Mix	0-15	13.8	67.4	0.0
Oct.		15-30	7.3	11.2	0.0
		30-60	7.4	3.1	
		60-90	5.4	4.1	
		90-120	3.4	5.3	
	Band	0-15	14.2	60.6	0.0
		15-30	10.0	7.3	0.0
		30-60	10.5	4.4	
		60-90	4.5	6.2	
		90-120	5.7	7.6	
3-6 Nov	Mix	0-15	8.9	90.3	0.0
		15-30	4.6	4.7	0.0
		30-60	5.7	8.3	
		60-90	1.8	3.6	
		90-120	3.2	5.2	

Table 13. Transformations of urea placed in nests in pots containing 500g, 1000g, 2000g and 4000g of soil. Samples of a Luvisolic soil were incubated at 24 °C and at 1/3 bar moisture. Urea was applied at a rate of 1.16g urea/pot. Values in µg N/g soil.

Pot size (g)	Time (days)	Urea-N	NH ₄ -N	NO ₂ -N	NO ₃ -N	NH ₄ /NO ₃	Recovery (%)
500	5	404.2	612.3	2.7	17.6	35.0	95.0
	10	0.0	860.6	10.3	55.9	15.4	84.0
	15		895.4	22.5	147.0	6.1	96.0
	20		790.5	14.6	218.4	3.6	92.0
	25		558.8	23.5	230.0	2.4	72.0
1000	5	205.1	322.4	5.6	11.1	29.0	98.9
	10	0.0	397.4	7.3	57.3	6.9	82.0
	15		409.8	11.7	110.3	3.7	94.0
	20		396.2	9.8	164.8	2.4	99.7
	25		258.4	9.7	167.4	1.5	75.0
2000	5	153.3	110.8	5.1	8.3	13.0	99.4
	10	0.0	187.6	8.5	27.4	5.8	75.6
	15		170.9	5.2	63.5	2.4	80.0
	20		165.3	6.7	96.8	1.7	88.0
	25		158.8	11.1	104.6	1.4	86.0
4000	5	31.7	97.3	5.0	8.3	12.0	99.0
	10	0.0	99.4	3.9	24.4	5.5	81.0
	15		84.8	3.5	48.3	2.0	89.4
	20		74.1	5.4	58.0	1.3	79.0
	25		57.1	6.1	63.8	0.9	71.0

Continue...

Control

5	0.4	0.0	8.4
10	0.4	0.0	14.4
15	0.7	0.0	24.9
20	3.2	0.0	27.7
25	2.1	0.0	29.5

Table 14. Transformations of urea placed in pots containing 500g, 1000g and 2000g of soil. Samples of a Black Chernozemic soil were incubated at 24 C and at 1/3 bar moisture. Urea was applied at a rate of 1.16 g urea per pot. Values in ug N/g soil.

Pot size (g)	Time (days)	Urea-N	NH ₄ -N	N ₂ -N	N ₂ O-N	NH ₄ /N ₂ O	Recovery (%)
500	5	325.0	659.7	7.0	29.3	22.0	92.0
	10	0.0	816.2	20.6	99.3	8.1	
	15		734.8	26.1	216.7	3.2	93.0
	20		637.5	32.6	221.4	2.9	
1000	25		474.8	27.1	347.2	1.3	75.0
	5	168.7	335.1	6.6	15.4	21.0	95.0
	10	0.0	440.9	20.1	74.5	5.8	
	15		363.6	16.4	160.3	2.2	94.0
2000	20		280.4	15.5	255.7	1.0	
	25		168.0	18.6	235.8	0.7	72.0
	5	135.1	124.2	2.3	13.1	9.5	
	10	0.0	166.8	5.9	37.5	4.3	
Control	15		136.2	9.0	81.2	1.5	72.0
	20		110.4	8.1	133.8	0.8	
	25		68.9	16.0	119.0	0.5	62.0
	5		0.7	0.0	10.2		
Mix *	15		1.8	0.0	32.2		
	25		1.8	0.0	33.8		
	5	0.0	4.6	0.0	28.3	0.2	70.0
	15		2.8	0.0	53.7	0.1	72.0
	25		1.8	0.0	52.6	0.0	60.0

* Urea was applied at a rate of 31.4 ug N/g soil